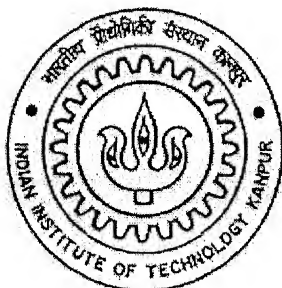


Studies on removal of pentavalent arsenic through Micellar Enhanced Ultrafiltration

*A thesis submitted
in partial fulfillment of the requirements
for the degree of
Master of Technology*

By
Rakhi D. Oli



to the
DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
JUNE 2004



CERTIFICATE

This is to certify that the thesis work entitled, “**Studies on removal of pentavalent arsenic through Micellar Enhanced Ultrafiltration**”, by Rakhi D. Oli has been carried out under my supervision and that it has not been submitted elsewhere for a Degree.

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Dedicated

to

MY PARENTS

&

BROTHER

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There is nothing more critical to the acquisition of most graduate and postgraduate degrees than the successful completion of one's own unique, independent research study. Clearly, anything as challenging and laborious as a thesis or dissertation can drain even the most able of minds. It is rare that anyone can expect to complete the entire process without any guidance, tutoring, or research assistance. It is for these very reasons that I would like express my heartfelt gratitude to **Prof. P. K. Bhattacharya**, my thesis supervisor and guide, for his valuable guidance in all the stages of the thesis work. His ingenious ideas and constant encouragement have helped me immensely in completing the research work. He had been involved in every aspect of this work, starting from the planning stage to the writing of this report. I would pay my gratitude to **Prof. Rajdip Bandyopadhyaya (my acting guide)**, who finally helped me to wind up my thesis work and guided me to the best of his knowledge and to **Prof. V. Shankar** for his support. I also pay my gratitude to aunty, Mrs. Bhattacharya.

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Rakhi Oli

Abstract

Arsenic removal being a worldwide problem today, attempt was made to study its removal by micellar-enhanced ultrafiltration in batch mode in unstirred pattern through 10000 MWCO ultrafilter membrane. The two-oxidation states of arsenic common in drinking water are trivalent [As (III)] and pentavalent arsenic [As (V)]. Pentavalent arsenic is thermodynamically stable form of arsenic in toxic water, and generally predominates in surface water. Therefore, the removal of As (V) was studied over wide a concentration range of 0.01- 14 mM. Exclusive runs for both the forms of arsenic were also carried out, which showed negligible effect of concentration polarization. During the initial period, a distinct drop in percent retention was observed because of initial adsorption of arsenic with the polymeric membrane. The retention of As (V) was found to be more as compared to the retention of As (III) at the same pH of 7.5.

The effects of feed surfactant concentration, metal ion concentration as well as the effect of pressure on the permeate flux and arsenate adsorption on the micelles (measured in terms of retention during UF) were also studied. As expected and interestingly, there was no variation of flux with time, which shows the negligible influence of concentration polarization, in presence of arsenate ions for all concentration values of CPC. However, with the increase in surfactant feed concentrations, flux values declines due to the formation of MAL. The removal patterns were different for different arsenate concentrations. For very low arsenic concentration (0.01 mM pentavalent arsenic) the percent removal remains almost same and constant. For the concentration of 0.1 mM, 1 and 5 mM arsenate, there is an initial increase in the percentage removal and then saturation was observed (as time proceeds). At very high arsenate concentration (14 mM) a perceptible decrease in percent removal was seen at the initial period after which more or less it remains constant. This may be because, adsorption may not be favored at such a high concentration of arsenic. The effects of pressure on permeate flux as well as on percent retention were also studied for a feed concentration of 0.1 mM of As (V) and 30 mM CPC concentration. The pressure influence of the arsenate adsorption on the membrane surface is being found negligible. However, as the pressure keeps on increasing, permeation of arsenic adsorbed on smaller sized micelles may be favored and hence may show a slight decline in percent retention. The equilibrium adsorption coefficient (K_{ad}) for arsenate ions were found out with the help of MEUF results. The value of K_{ad} was found to vary with the feed surfactant concentration.

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Nomenclature

a	molar extinction coefficient ($\text{mole}^{-1}\text{l}^{-1}$)
A	membrane area (m^2), absorbance
C	concentration (mole/l)
D	diffusivity (m^2/s)
ΔS^0	standard enthalpy of micellization
ΔH^0	standard heat of micellization
f	activity coefficient
G	free energy (J/mole)
H	enthalpy (J/mole)
J	permeate flux (m/s)
L	cell path length
M	molecular weight (g/mole), micelles
N	aggregation number
P	pressure (kPa)
R	gas constant (J/mole-K), resistance (m), rejection
S	entropy (J/mole-K)
t	time(s)
T	absolute temperature (K)
K_{ads}	Langmuir adsorption equilibrium constant.
V	volume (m^3)
z	distance from the membrane surface

Greek letters

Δ	difference
λ	wavelength (nm)
μ	viscosity (Pa-s)
ν	kinematic viscosity (m ² /s)
π	osmotic pressure (kPa)
ρ	density (kg/m ³)
ϕ	association factor

Subscripts

ads	adsorption
b	bulk
c	hexavalent chromium
eq	equilibrium
f	feed, fouling
j	component
m	membrane
ma	mass action
M	micellar phase
o	observed, initial
p	permeate
ps	phase separation
r	real
s	surfactant
w	water

Superscripts

B	blank (exclusive)
0	standard states

Abbreviations

Amp	ampere
CFC	critical feed concentration
CMC	critical micellar concentration
CPC	cetyl pyridinium chloride
CTABr	cetyl trimethyl ammonium bromide
conc.	concentration
Hz.	Hertz
MAL	micellar aggregation layer
MEUF	micellar enhanced ultrafiltration
SDS	sodium dodecyl sulphate
SED	semi equilibrium dialysis
soln.	solution
MCL	maximum contaminant level

Chapter 1

Introduction

Increasing contamination of industrial wastewater by toxic inorganic pollutants is a serious environmental problem. These inorganic pollutants are of considerable concern as many are non-biodegradable, toxic and have a probable carcinogenic effect. Further, if recovered, these chemicals may prove valuable to save recurring cost of the plant. Industries have, therefore, always attempted through developing technologies to meet such objectives. The common approach has been to either treat these effluents to facilitate easy disposal, or to recover the chemicals and recycle the processed water.

Arsenic is the 20th most abundant element in the earth's crust; whereas, it is the 12th most abundant element in the human body. Arsenic is known as a poison if ingested in too large a dose; whereas, in smaller quantities taken over a long period, it is known to have a carcinogenic effect. Extensive arsenic contamination of surface and groundwater has been reported in many parts of the world [1]. This arsenic contamination invariably arises from natural geological and environmental conditions. Arsenic arises in many ores and minerals and is frequently present in combination with iron and manganese oxides; under various natural conditions, it can be rendered soluble and released into the groundwater. In many parts drinking water is contaminated by arsenic percolating from mining and refinery waste or traceable to arsenic containing pesticides. Occurrence of arsenic is in varieties of forms and oxidation states. The two oxidation states common in drinking water are trivalent As (III) and pentavalent As (V). Pentavalent arsenic is thermodynamically stable form of arsenic in toxic water, and generally predominates in surface water. The possible long term effects and the risks associated with the ingestion of arsenic contaminated water have compelled the regulatory agencies to promulgate a lower standard for arsenic in drinking water. The world health organization (WHO) recommends 10µg/l for arsenic concentration and United States Environmental protection agency (USEPA) also adopted this arsenic standard for drinking water [2]. Arsenic level in water as per the Indian / Bangladesh

standard is 50µg/l. Hence it becomes imperative for the industries, generating arsenic, as well as for the environmentalists to look for attractive methods, other than the conventional methods for its disposal and/or use.

The use of membrane separation processes, in the treatment of wastewater containing toxic inorganic chemicals, is an attractive and suitable technique, and it may easily be integrated with the whole process; which is why the membrane separations are being used more frequently [3]. Two types of membrane separation processes have been demonstrated to be effective in removing arsenic from water. Reverse osmosis (RO) or nano-filtration (NF) may be a suitable proposition apart from electrodialysis (ED). With As (V) as feed, removal rates greater than 97% are reported by RO processes. Electrodialysis is another type of membrane water treatment process where an electric current is applied to draw the ions (dissolved solids) through the membrane leaving the “fresh” water behind. The membrane separating the ED unit is made up of cation and anion exchange resin [2]. In RO pressure is applied on the “salty” side of a RO membrane to force “fresh” water through the membrane thereby concentrating the dissolved solids on the “salty” side.

Ultrafiltration (UF) is one of the most effective methods of concentrating and fractionating macromolecular solutes. However, with some modifications organic compounds as well as metal ions (upto 1000 Da) from aqueous streams may also be separated. Separation is primarily through sieving action which is based on the size fractionation through micro-porous UF membranes. But it is not an appropriate method to seek separation for solutes differing marginally in size or for solutes in ionic size. In this regards micellar enhanced ultrafiltration (MEUF) [3-9], is proving to be an effective technique in removing solutes which have insignificant retention in an otherwise through UF. In MEUF, as shown in a schematic in Fig 1.1, surfactants (MW ~ 250 to 800) form aggregates (large amphiphilic groups) of micelles above the critical micelle concentrations (CMC), and this micellar pseudo-phase can be regarded as a receiving phase for some solutes in a manner similar to organic solvents in a conventional liquid-liquid extraction. If the tendency for the metal ion to be attracted on the micelle surface or for the organic molecules to be solubilised in the micelle interior is strong, a large

fraction of the metal ions or dissolved organic molecules are trapped by micelles. Such a solution upon UF permeates (through a chosen molecular weight cut off size of the membrane) monomer surfactants and retains the micelles along with the bound ions (or organic solutes), since the size of surfactant micelles is usually large enough (MW – 20,000 to 150,000). The permeating solution may contain a low concentration of the metallic ions or organic solutes. The binding force between micelles and solutes (to be recovered) is responsible for effective MEUF operation. However, selective removal of metal ions, having similar electric charges, can not be expected since the main binding force is due to the electrostatic attraction. Theoretically, the metal ion concentration in the permeating solution should be equal to or less than the concentration of the unbound ions in the retentate. Similarly, the surfactant concentration in the permeating solution may be found equal to or less than the surfactant monomer concentration in the retentate. As either of these two concentrations are low, the permeating solution thus obtained may be of high purity. The retentate stream can then be treated for the recovery of the metallic ion and the surfactant.

Multivalent metal ions have been successfully recovered through MEUF using surfactants having the opposite charge. Very typical anionic and cationic surfactants are sodium dodecyl sulfate (SDS) [4, 5] and cetyl pyridinium chloride (CPC) [6, 7], respectively. The process is versatile enough to include the removal and recovery of various organic acids and amines, separation of hydrocarbons, apart from the separation and concentration of a large number of metal ions.

In the design of MEUF process, the effect of operating parameters on the efficiency of the process, permeate flux and retention of micelles along with metal ions and quality of permeate concentrations are to be properly understood. Markels et. al [8] carried out MEUF in an unstirred batch cell and had proposed an unsteady state mass transfer model to describe the retention characteristics of the membrane. The model helps to estimate the intrinsic retention for both, the surfactant and organic solute and describes the physics at the membrane surfaces. Markels et. al [9] had also conducted crossflow ultrafiltration of micellar solutions. A steady state fouling resistance and osmotic pressure model was proposed by them to predict flux in cross flow MEUF process.

The selection of surfactant is made on the basis of the extent of solubilisation of organic solute or adsorption of metallic ions on the surface of the micelles. It is seen that the surfactant having charge opposite to that of the target ions has higher efficiency in entrapping the solute or metal ions. The binding of hydrophobic solutes to both ionic and nonionic solutes were considered and was shown to be a function of the molecular structure of the surfactants, the concentration of the surfactant and the electrolytic composition of water [10]. An earlier attempt [11] was made using a cationic surfactant, CPC, for the removal of an anionic solute, both ionic and nonionic, the study of their behavior in a particular surfactant may be of interest for convenient design.

In the present work, an attempt has been made to study the adsorption of pentavalent arsenic [As (V)] on the micelle surface and thus observe its removal. Accordingly, in this work, cetyl pyridinium chloride (CPC) was chosen as a cationic surfactant for the formation of micelles in order to observe adsorption/removal of pentavalent arsenic ion for which sodium arsenate (which gives anionic solute) in a medium of 0.01 M sodium chloride (NaCl) solution was taken.

Based on the above introduction, following broad objectives were laid down to conduct a predominant experimental study:

1. To fundamentally study the permeate flux and retention patterns against distinct operating conditions with exclusive runs of As (V) solution
2. To study the effects of As (III) and As (V) species on the percent retention and permeate flux.
3. To study the influence of operating conditions (concentration of surfactant, concentration of pentavalent arsenic, pressure and time) on permeate flux and respective retentions/removals of pentavalent arsenic
4. To observe the amount of adsorption of arsenate on micelles against operating conditions and to calculate the adsorption coefficient.

Micellar Enhanced Ultrafiltration

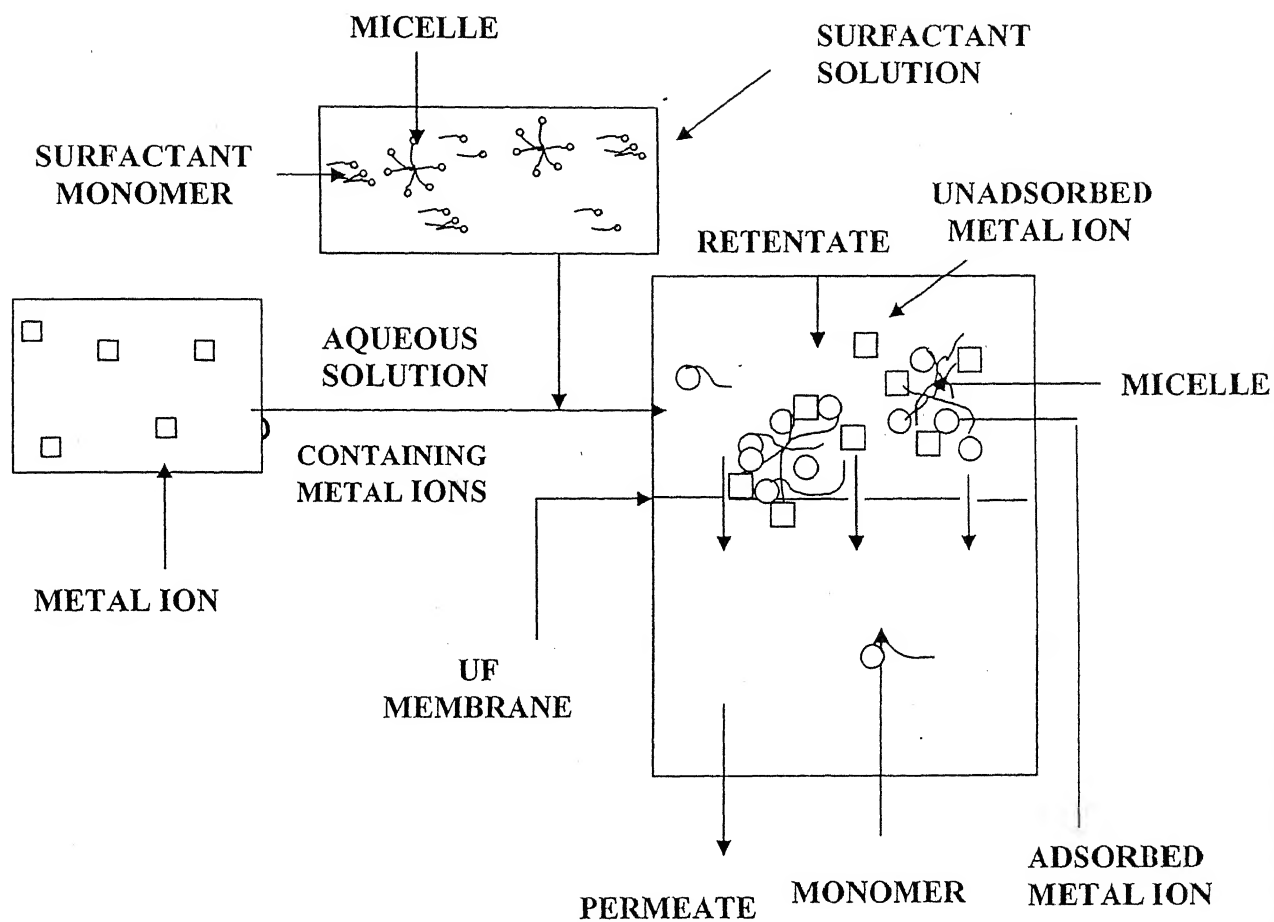


Fig. 1.1- Schematic of Micellar Enhanced Ultrafiltration to remove dissolved metal ions from water

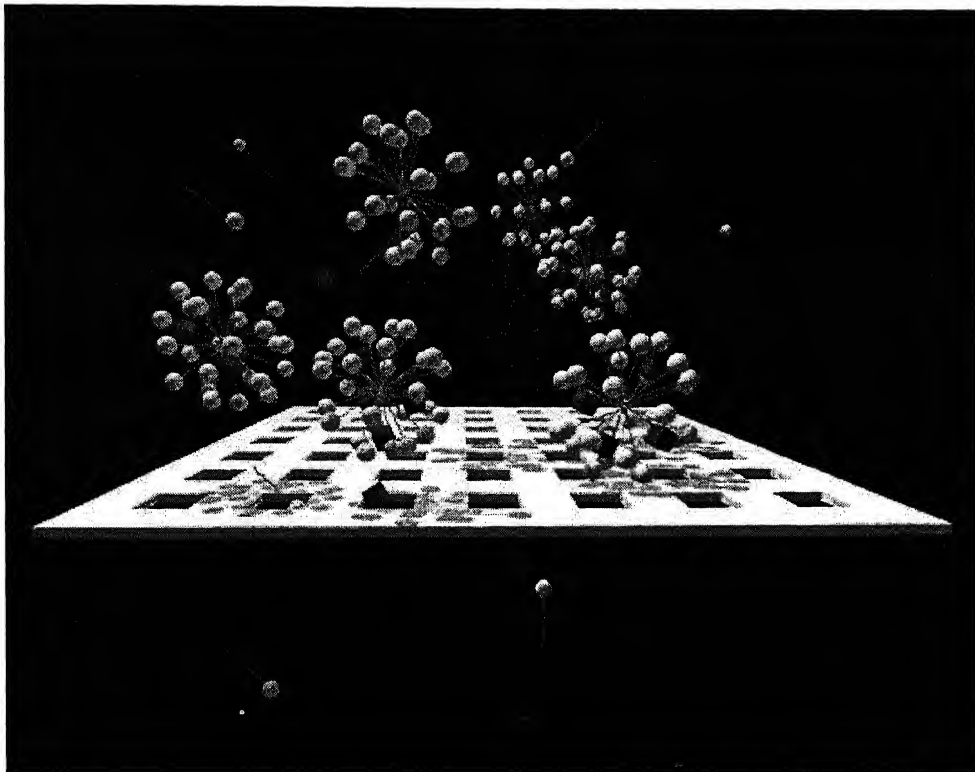


Fig. 1.2 – 3-D Visualization of Micellar Enhanced Ultrafiltration across the membrane surface

2.1 Separation Processes for the removal of Metal ions from Aqueous Stream

With continuing stringent environmental regulations, disposal of a large volume of waste water containing even trace quantities of toxic metal ions and organic solutes has recently drawn considerable attention. While a number of separation methods such as liquid extraction, activated carbon adsorption, ion exchange method, cellulose xanthate, electrolytic method, hydroxide precipitation, sulphide precipitation are applied they all have some innate disadvantages. These processes often require expensive reagents, led to large volumes of sludge generation, lose of expensive chemicals to waste water, are frequently energy intensive, and may still be ineffective at reducing pollution concentration to environmentally safe levels [12]. Among this sludge generation and disposal is the most pressing problem.

Activated Carbon Adsorption

Activated Carbon Adsorption is an emerging technology for removal of inorganic species from wastewater such as cyanides, heavy metal ions, etc. Adsorption is defined as the collection of a substance onto the surface of adsorbent solids. It is the removal process where certain particles are bound to an adsorbent particle surface by either chemical or physical attraction. The activated carbon is an effective adsorbent material due to its large number of cavernous pores, which provide a large surface area. However, the maximum adsorption capacity of carbon is much pH sensitive and decreases rapidly with the change in pH.

Activated carbon is expensive and need to be regenerated. The regeneration and disposal of carbon containing metal ions is by itself a problem. Moreover, this process fails to produce an effluent with metal ion concentration at per with wastewater disposal norms, especially if the concentration of metal ions in the feed is high.

Ion Exchange Process

Ion exchange is a reversible chemical reaction wherein an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. The synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications.

Following is the selectivity sequence of an anion exchange resin:

citrate>sulphate>oxalate>iodide>nitrate>chromate>bromate>SCN>chloride>formate>acetate>fluoride>hydroxide.

Even though, ion exchange is suitable for treatment or materials recovery from very dilute solutions, the process is expensive as ion exchange resins and regenerating chemicals are costly, in addition this process is inapplicable to wide pH range.

Modified Activated Carbon Adsorption

Modified activated carbon is carbonaceous adsorbents which have tetrabutyl ammonium iodide (TBAI) and sodium diethyl dithiocarbamate (SDDC) immobilized at their surface. This modified adsorbent used for the adsorption of toxic ions, copper, chromium, zinc and cyanides in wastewater. This modified technique enhances the removal capacity of carbon and therefore decreases cost-effective removal of Cu(II), Zn(II), Cr(II) and CN⁻ from wastewater. The TBA-carbon modification has a cyanide removal capacity of approximately five times to that of plain carbon. The SDDC-carbon showed Cu, Zn, Cr removal capacity from two to four times higher to that of plain carbon. The removal of these metal ions follow a descending order pattern [13], Cu>Zn>Cr. In this also regeneration and disposal of carbon, containing metal ions, is problem.

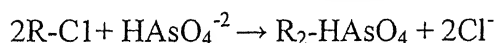
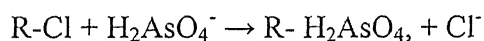
2.2 Separation Processes for the Removal of Arsenic (V)

Removal of Arsenic-V by Adsorption on Activated Carbon

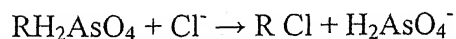
As (V) is more effectively removed from solution by using activated carbon with a high ash content. Pretreatment of the carbon with Cu (II) solutions improves its arsenic removal capacity. The optimum pH for arsenic adsorption by pretreated carbon is approximately 6. There are two mechanisms of arsenic adsorption which occur simultaneously. The arsenic in solution can form insoluble metal arsenates with the copper impregnated in the carbon. Arsenic is also adsorbed independently of the impregnated copper. Ion pair formation has been ruled out in the latter case. Arsenic desorption is easily achieved using strong acidic or alkaline solutions. When acidic solutions are used, copper is also eluted [14]. Further in this procedure desorption is to be carried out and the adsorbent used is to be regenerated which makes the process highly expensive.

Removal of Arsenic from drinking water by Anion Exchanger

In neutral solutions (pH 6.5-8.5), the trivalent form is found as H_3AsO_3 ($\text{P}k_1 = 9.22$, $\text{P}k_2 = 12.3$, $\text{P}k_3 = 13.4$) and the pentavalent form as H_2AsO_4^- ; and HAsO_4^{2-} ; ($\text{P}k_1 = 2.2$, $\text{P}k_2 = 7.1$, $\text{P}k_3 = 11.5$). Strong-base anion-exchanger resin absorbs arsenic ions from water according to the following reactions:



As the selectivity of such resin to divalent anions is higher than its selectivity to monovalent anions, the efficiency of the process at high pH, under which the proportion of divalent arsenic anions in the water is greater, may be expected to be higher too. Regeneration is carried out with excess of chloride ions in the following reaction:



Although it is possible to eliminate over 99% of the As in drinking water by this method the method is not efficient when sulfate, chloride and other anions are present in the water in high concentrations. The regenerant solution contains a high concentration of As and could therefore pose a serious environmental problem. Recycling and disposal of the waste produced is also a problem [15].

Removal of Arsenic (V) with a Ce (IV)-doped iron oxide adsorbent

The removal of arsenic (V) by a new Ce-Fe adsorbent was evaluated under various conditions. Under an initial As (V) of 1.0 mg l^{-1} , the adsorption capacity of the Ce-Fe adsorbent was constant around a value of 16 mg g^{-1} over a wide pH range (3–7), while a maximum adsorption capacity of 8.3 mg g^{-1} was obtained over a narrow pH range around 5.5 for activated alumina, a conventional adsorbent. Kinetics of adsorption obeys a pseudo-first-order rate equation with the rate constant K_{ad} as $1.84 \times 10^{-3} \text{ min}^{-1}$. The pattern of adsorption of As (V) by the adsorbent fitted well both the Langmuir and Freundlich models. A Langmuir Q_0 of 70.4 mg g^{-1} was obtained at an initial pH of 5.0 and temperature of 20°C , significantly higher than those of other adsorbents reported [16].

Removal of arsenic (III) from groundwater using fixed-bed up flow Bioreactors

The objectives of this research were to examine whether trivalent arsenic can be efficiently treated, without any additional use of chemicals and to investigate the effect of the main parameters, which affect As (III) removal, leading to better understanding of the removal mechanism. The objectives of this research were to examine whether trivalent arsenic can be efficiently treated, without any additional use of chemicals and to investigate the effect of the main parameters, which affect As (III) removal, leading to better understanding of the removal mechanism. This work was based on Fe (II) and Mn (II) oxidation by *Gallionella ferruginea* and *Leptothrix ochracea*. The products of biological oxidation are iron precipitates, which are in most cases slightly hydrated iron oxides, especially lepidocrocite and sometimes goethite they are considered as effective adsorbents for subsequent As (V) and As (III) removal [17]

2.3 Membrane Separation processes for the separation of Arsenic Species

The challenge that the maximum contaminant level (MCL) for arsenic will be reduced substantially appears to meet through the novice membrane separation techniques. Membrane technologies for water treatment have been vastly improved in areas of water flux, salt rejection, and especially in their ability to maintain high performance levels at substantially lower operating pressures than the predecessors. One of the few studies evaluated a variety of membrane processes for their ability to reject arsenic under a range of conditions. The successful application of membrane technology to the removal of arsenic from drinking water will depend upon matching the proper membrane to the characteristics of the source water. Table 2.1 outlines the suitability of several membrane treatment options when matched to characteristics of arsenic in the source water. The treatment options are divided into two classes, membrane filtration alone, and membrane filtration preceded by pretreatment. Membrane treatments are subdivided into the four major membrane classes, RO, NF, UF and MF. Preoxidation is considered as a pretreatment. Three characteristics of the source water are also considered. These are the speciation of the arsenic present in the water, the size distribution of the arsenic in the water and the co-occurrence of organics or inorganics in the water. The relative applicability of the various treatment options is as indicated

Source Water Characteristics	Treatment Option				Possible
	Filtration alone				Pretreatment
	RO	NF	UF	ME	Preoxidation
<i>As Speciation</i>					
As (III)	R	P.E	N.R	N.R	R
As (V)	R	R	P.E	N.R	N.R
<i>As Size Distribution</i>					
Dissolved	R	P.E	N.R	N.R	N.R
Particulate	N.R	N.R	P.E	P.E	N.R
<i>Co-occurrence</i>					
NOM	P.E	P.E	N.R	N.R	N.R
Inorganic	R	P.E	N.R	N.R	N.R

R: Recommended, R.O: Not Recommended, P.S: Possibly Effective.

The membrane separation processes which are useful for the purpose are described below with their importance.

2.3.1 Removal of Arsenic by nanofiltration

When a solution containing ions is brought in contact with membranes possessing a fixed surface charge, the passage of ions possessing the same charge as the membrane (co-ion) can be inhibited. This condition is termed Donnan Exclusion. More specifically, when a solution with anionic arsenate is brought in contact with a membrane possessing a fixed negative charge, the rejection of arsenate may be greater than if membrane was uncharged. Hence the membrane possessing a slight negative charge may be advantageous for the removal of arsenic from drinking water. This is a particularly fortunate set of circumstances, since most NF and UF membranes possess a slight negative charge, and the speciation of arsenic in natural waters is primarily in the anionic arsenate form [18]. Application of NF to drinking water treatment for arsenic removal was examined with a negatively charged NF membrane. Experiments were conducted with ground water to which arsenate, arsenite and DMMA were added. Arsenate rejection was almost steady, while rejection of arsenite increased with pH. Compared to the rejection of chloride ion, arsenic compounds except DMMA generally gave lower rejection. The reason for rejection change with pH was explained by the extended Nernst-Planck equation which showed that electrically charged membranes generally have a higher rejection for charged solutes than for non-charged solutes. The arsenate As (V) was either in monovalent anion or in divalent anion through all the pH range investigated. The rejection of arsenate was increased with increase in pH from 87% at pH 3 to 93% at pH 10. The degree of increase with pH in arsenate case was smaller compared to the case of arsenite. Low pressure operation of the NF process is advantageous in energy consumption. Normal NF processes are operated at around the 1 MPa range. Low pressure operations, as low as 0.1 MPa induce a larger application of the NF process. One problem in lower pressure operation is that the rejection in the case of reverse osmosis (RO) and NF decreases in the case of low pressure operation. Difference in rejection of

different solutes becomes larger in low pressure operation compared to the case of high pressure operation of high rejection RO membranes. Nominal rejection of the NF membranes is often characterized by sodium chloride rejection. It is not definite that the high rejection membranes in terms of sodium chloride always give high rejection against arsenic compounds because the rejection of NF is dependent on molecular charge of the solutes, molecular size of the solutes, etc. [19]. In another study the effectiveness of NF processes were discussed over the conventional coagulation process. Soluble form of arsenic and iron were not removed by inter-chlorination and manganese sand filtration whereas they showed 95% removal of pentavalent form of arsenic and 75% of trivalent form of arsenic removal without any chemical additives [20].

2.3.2 Removal of Arsenic by reverse osmosis

Two types of RO membranes, ES-10 and NTR-729HF, were used to study the removal of both arsenates (As-V) and arsenites (As-III) from drinking water [21]. Permeate flux was relatively low for the NTR-729HF compared to the ES-10 which has a higher flux. The removal of arsenate was higher than that of arsenite over the pH range of 3 to 10 investigated in this study. The removal of arsenic compounds is almost proportional to the removal efficiency of sodium chloride. The removal of arsenite by ES-10 was more than 75% through all the pH range investigated, while the removal by NTR-729HF was lower than 43 %. The removal of arsenite was increased sharply as the pH increased from 7 to 10. It shows that the effect of solution pH affects the removal of arsenite because most of the arsenite exists in monovalent anion form at pH 10, while most of the arsenite exists in a neutral molecule at pH 3, 5 and 7. The removal of arsenate by ES-10 was more than 95% through all the pH range investigated.

2.4 Micellar Enhanced Ultrafiltration (MEUF)

Micellar Enhanced Ultrafiltration can be used to remove dissolved multivalent ions from water [22]. An appropriate concentration of surfactant of opposite charge to that of the ions is added to the aqueous stream, so that a large fraction of the surfactant exists in the micellar form. The target ions get bound or adsorbed on the micelles due to electrostatic attraction. When the resulting solution is passed through an ultrafilter having

pore diameters smaller than micelle diameter, most of the surfactant and metal ions entrapped in micelles remain in the retentate solution. The permeate solution passing through the membrane is in many cases practically pure water [9]. This process can also be used for the separation of hydrocarbons and removal and recovery of organic acids, alcohols, and amines [22].

2.4.1 Removal and Recovery of Organic Solutes

MEUF results for the removal of 4 tert-butyl- phenol (TBP) using CPC as surfactant were reported for membranes with pore sizes ranging from 1000 to 50,000 MWCO [22]. The removal of n-alcohols and cresols by MEUF using CPC as the surfactant was also reported [23]. The effects of retentate CPC concentration on permeate flux and permeate CPC concentration was studied [4]. Experimental work on micellar ultrafiltration of CPC solution in batch cell at constant flux was also carried out [8].

Separation of phenol and 4-nitrophenol by means of hexadecyl-trimethylammonium bromide (CTAB), sodium dodecyl sulphate (SDS), alkyl polyglucoside (APG) and oxyethylated methyl dodecanoate (OMD) from water and NaHCO_3 solution was reported [24]. The approach has been made to evaluate the resistance of secondary layer and its change as a function of flux, time and the effect of pollutants and modifiers.

MEUF was applied to mixtures containing phenol or 0-cresol and simultaneously, Zn^{2+} and / or Ni^{2+} , using an anionic surfactant [25]. The results demonstrated that removal of organic solute was not significantly affected by the presence of metal ions and vice - versa. This is because, the predominant mechanism of removal of metal ions were totally different. The ability of MEUF to simultaneously remove organic and multivalent metal ionic solutes makes it economically attractive.

The effect of important operating parameters (applied pressure, concentration of solutes and surfactants) on the extent of separation of organic solutes (aniline and phenol) was observed [26]. Solubilisation of these solutes in CPC micelles was experimentally ascertained. Solubilisation equilibrium constant of phenols in CPC was estimated to be around four times that of aniline. A mathematical model developed in this study [26] was used to describe the separation of organic solutes by MEUF and predict permeate solute

concentration under varying operating conditions. Equilibrium distribution constants of phenol between surfactant micelles and water were determined by MEUF using commercial ultrafiltering centrifuge tubes [27]. Three surfactants: sodium dodecyl sulphate (SDS), polyethylene 20 cetyl ether (C16E20) and cetylpyridium chloride (CPC) were tested with a 10,000 MWCO membrane.

A steady state combined resistance in series and osmotic pressure model was proposed [7] to predict the flux in laminar, cross flow ultrafiltration of micellar CPC solution. The data were obtained for CPC monomer-micellar equilibrium in aqueous solutions using UF [28].

2.4.2 Separation and Concentration of Metal Ions

The application of MEUF for removing heavy metal ions from water is getting noticed [28]. MEUF was found to be extremely effective in separating Cu^{2+} and a rejection of 99.8% was observed when present in dilute concentration [29]. However, the permeate purity decreased as the metal concentration in the feed increased. Further, purity also gets affected by the reduction in surfactant concentration and or with the presence of monovalent salt in the solution.

MEUF of gold (III) from hydrochloric acid media was also studied [30] using polyoxyethylene nonylphenyl ethers (PONPES) as a nonionic surfactant. The rejection efficiency of gold (III) increased with increasing surfactant concentration, ethylene oxide number of PONPE and the applied pressure as well as decreasing molecular weight cut-off of the membrane. It was found that the use of MEUF with PONPE provides higher selectivity to gold (III) than those with charged surfactant such as cetyl pyridinium chloride (CPC) and sodium dodecyl sulphate (SDS).

Traces of aluminium were preconcentrated [31] in water by forming a complex with lumogallion. Thereafter, it was successfully accumulated in the micellar phase, obtained from cationic and non-ionic surfactants, and filtered through 10,000 MWCO ultrafiltration membranes. It was reported [31] that at pH 5.9, with 1×10^{-3} M lumogallion and 2×10^{-2} M cetyltrimethylammonium bromide, quantitative retention of aluminium present at $\mu\text{g/ml}$ concentration level was achieved.

Lecithin, a natural, nontoxic, and biodegradable surfactant exhibits emulsifying characteristics, which may be used for MEUF. The binding of various lecithin to cadmium, copper, lead, nickel and zinc in a mixture as well as individually were observed [32]. In the presence of all five heavy metals, the lecithin showed the higher affinity for Cu than for Cd and Zn whereas Ni was found to have the lowest affinity. The affinity for Cd and Zn were found to be similar. In experiment when only one metal was present, lecithin exhibited the following affinity: $Ni > Cu$ and $Zn > Cd$; whereas Cu and Zn show similar affinity. Lead was not bound significantly in the either scenario.

Industrial wastewater from metal plating, petroleum refining, chemical and food processing plants vary in composition and may contain toxic substances like heavy metal cations and chemical compounds in the aqueous phase and oil fractions. It had been proposed [33] to combine MEUF and algae containing membrane bioreactors (MB) to completely remove the metal ions from metal finishing industry's effluent. MEUF, with lecithin as surfactant, was found to remove heavy metals from aqueous (50 – 90% removal) and non aqueous wastes (90 -97% removal). Continuous binding and separation of the ions through membrane bioreactors that were 20 -50 times more efficient than conventional bioreactors, increased the efficiency of removal of trace levels of heavy metals.

The removal of hexavalent chromium by micellar enhanced ultrafiltration using cetyl trimethylammonium bromide (CTABr) as well as cetyl pyridinium chloride (CPC) were experienced [34, 7]. Effect of metal ion concentration, surfactant concentration, presence of monovalent salt against varied transmembrane pressure drop, feed velocity and temperature were studied. Rejection coefficients, higher than 99%, were obtained as long as the feed concentration is less than or equal to 200 times the standard. The rejection rate was found to depend on ionic strength and pH. The increase of ionic strength decreased the retention of chromate ions and permeate surfactant concentration. As long as the NaCl feed concentration was less than or equal to 100mM, more than 88% of hexavalent chromium were retained and surfactant leakage was reduced [34, 7]. Addition of small concentration of nonionic surfactant to anionic surfactant results in anionic nonionic mixed micelles and exhibit negative deviation from ideality of mixing.

This leads to smaller fraction of surfactant being present as monomer and subsequently a large fraction present in micellar form [12]. It was reported that addition of nonionic surfactant improved the separation of Zn^{2+} substantially at total concentration above CMC of anionic surfactant. Both Zn^{2+} and tert-butyl phenol showed unexpected rejection at surfactant concentrations moderately below the CMC. This was considered to be due to a higher surfactant in the gel layer, adjacent to the membrane where micelles were present.

A lab study was conducted to evaluate the effects of composition and concentration of mixed anionic / nonionic surfactants on the study of MEUF operation for the removal of metal ions / organic solutes from aqueous solution [35]. Based on the analysis of surface tensions and micelle sizes, it was found that for mixed sodium dodecyl sulphate (SDS) / Triton X-100 surfactants, the CMC was significantly lower than that of SDS and formed mixed micelles. The rejection of Cu^{2+} was found to be negligible with a surfactant concentration 10mM, on using pure Triton X-100. Whereas the rejection increased upto 85% on increasing the SDS mole fraction, indicating the mechanism of Cu^{2+} rejection being chiefly due to the electrostatic attraction [12]. When MEUF technique was applied to Cu^{2+} and phenol simultaneously from aqueous solution, Cu^{2+} rejection was slightly enhanced in the presence of phenol [35]. However, rejection of phenol was comparatively low approx. 27%.

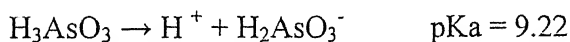
2.4.3 Miscellaneous Applications of MEUF

Micellar Enhanced Ultrafiltration was used to recover thuringiensin from the supernatant of *Bacillus thuringiensis* fermentation broth using CPC [36]. On manipulating various possible process variables, it was found that CPC concentration and membrane pore size were the two major factors to the increase recovery of thuringiensin. It was also reported that ionic strength, pH adjustments were not necessary and micelle formation temperature was not important within the temperature range studied. The bioassay results showed that the spray- dried thuringiensin with CPC was more toxic to fly larvae than without CPC. This indicates that CPC not only facilitated thuringiensin recovery but also improved the insecticidal effect.

In ligand modified MEUF (LM-MEUF), a surfactant and ligand are added to an aqueous solution containing ions of like charge. The ligand forms complex with the target ions and becomes incorporated in the micelles. An economic analysis of LM-MEUF for 1×10^5 gal/day unit is reported [37]. The effect of important parameters including feed surfactant, ligand and copper concentration were studied. The result from the sensitivity analysis was used to compare the cost of removal and recovery of copper between the processes of LM-MEUF and solvent extraction process. The comparative economic analysis indicated a 17% higher capital and 43% higher operating cost for LM-MEUF process compared to solvent extraction process [36].

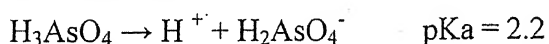
2.5 Chemistry of Arsenic

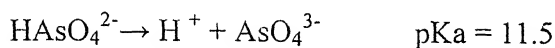
Arsenic, atomic number 33, is in the group VB of the periodic table, directly below phosphorous. Arsenic is considered metalloid and occurs in a variety of forms and oxidation states. The two oxidation states common in drinking water are arsenate As (V) and arsenite As (III). Both arsenate and arsenite are part of the arsenic (H_3AsO_4) and arsenous (H_3AsO_3) acid systems respectively [18]. Hence the pH of the system will control the degree of protonation of the acids. Arsenate is the thermodynamically stable form of inorganic As in toxic water, and generally predominates in surface water. The chemical equilibrium of arsenic compounds is shown below. Both arsenite and arsenate occur in several protonate forms as shown in Table 2.2; at near-neutral pH, the predominant species are H_3AsO_3 for arsenite and H_2AsO_4^- , and HAsO_4^{2-} for arsenate. Groundwater is often reducing (negative ORP). In reducing waters, arsenic is found primarily in the trivalent form (As- III) as some form of arsenious acid which ionizes according to the equations [15]:



(pKa is the pH at which the disassociation of the reactant is 50% complete.)

Pentavalent arsenic is normally found in water as arsenic acid which ionizes according to the equations:





This means that arsenate exists as an anion at typical pH (5-8) in natural water, while arsenite remains as a neutral molecule at the same pH region. Arsenite is proposed to have one negative charge at a pH over 9.2 [21]. Experience has shown that trivalent arsenic is difficult to remove from water using the normally available treatment processes. It is usually necessary to change the arsenic to the pentavalent form by adding an oxidant, generally chlorine.

S (III)	H_3AsO_3		H_2AsO_3^-		HAsO_3^{2-}
	H_3AsO_4	H_2AsO_4^-	HAsO_4^{2-}	AsO_4^{3-}	
S (V)	2.26	6.77	9.17	11.5	13.5

2.6 Structure of Surfactants

Surfactant is a diminutive term for SURFace ACTive AgeNT. Surfactants are materials that tend to not only accumulate at the surfaces or aggregate in solutions, but by their presence, they also change the properties of surfaces and solutions. More generally, they are active at the interfaces. Surfactant molecules have two distinct parts as shown in Fig. 2.1: one that has an affinity to the solvent (hydrophilic in case of aqueous solution) and the other that does not have any affinity (hydrophobic). It is the tendency of the hydrophobic part of the molecule to aggregate because of their mutual dislike for solvent. This dislike tends to become the driving force for the surfactant self – association. The hydrophilic head groups remain spaced out in the solution. The properties of surfactants fall into two broad categories: adsorption and self – assembly.

Adsorption is the tendency for a surfactant molecule to collect at the interface. This molecular property leads to the macroscopic properties of wetting, foaming, and emulsion formation.

Self – assembly is the tendency for the surfactant molecules to organize themselves into extended structures in water. This includes the formation of micelles, bilayers and liquid crystals.

Surfactant can be broadly classified into ionic, nonionic and zwitter ionic classes. Ionic can be both anionic and cationic surfactants [38].

Anionic Surfactant

This type of surfactant on dissociation in a liquid form results in a negatively charged ion. Commonly used anionic surfactants are alkyl sulfates, alkyl benzenesulfonates, alkyl sulfonates and the alkyl phosphates. In fact, probably the most studied surfactant over the years is one of the alkyl sulphates: sodium dodecyl sulphate. Anionic surfactants are widely used. They are used in shampoos, in dishwashing detergents and in washing powders. In many industrial and commercial applications, they are used in conjunction with nonionic surfactants to provide even greater stability.

Cationic Surfactant

This type of surfactant on dissociation in a liquid form results in positively charged ion. Alkyl pyridinium and quarternary ammonium salts provide excellent surfactants that can be used over a range of conditions. Cetyl pyridinium chloride and cetyl trimethyl ammonium bromide are the most commonly used cationic surfactants. They are used in things like hair conditioner and fabric softeners. The fatty amine salts are quite useful along with nonionic surfactants, giving good stability over a range of pH levels.

Zwitter ionic or Amphoteric Surfactant

This type of surfactant contain both positive (cationic) and negative (anionic) groups. In acidic solutions they form cations and in alkaline solutions they form anions. Whereas, in the middle range of pH they become molecules with two ionic groups of opposite charges known as Zwitter ions. The key property of amphoteric surfactants is the compatibility with aqueous ions and being resistant to both acids and alkalis. Therefore, they are often used for foaming, wetting and emulsification in personal care products.

Non-ionic Surfactant

This type of surfactant on dissociation in liquid form does not result in either positively charged or negatively charged ions. They are referred chiefly to polyoxyethylene or polyoxypropylene derivatives. However, other surfactants are also

included such as, fatty alkanoamides and amine oxides. They are usually prepared by addition of ethylene oxide to alkyl phenols, fatty acids and alcohols, fatty mercaptans and amines [39].

Another class of nonionic surfactants is alkyl polyglycosides. At least, for the last 20 years, these have been dubbed the “new generation nonionic surfactants”. In these molecules, the hydrophilic group is sugar. Alkyl glycoside and glucose ester are examples of alkyl polyglycosides.

Nonionic surfactants differ from both cationic and anionic surfactants in that the molecules are actually uncharged. The hydrophilic group is made up of some other very water-soluble moiety, (e.g. a short, water-soluble polymer chain) rather than a charged species. Traditionally, nonionic surfactants have used polyethylene oxide chains as the hydrophilic group. The predominant use of these surfactants is in food and beverages.

Nonionics do not contain ions and hence solubilise over the pH range. Their solubility is due to hydrogen bonding between the hydrophile and water molecules. Amphoteric have both anionic and cationic groups, so they are soluble in water over wide pH limits; even wider than nonionics. Whereas, nonionics lose their solubility at low and high pH, and at high electrolyte levels, as electrolytes competes with ethoxylate chain for hydrogen bonded water [40].

pH	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Anionic														
Nonionic														
Cationic (weak)														
Cationic (quat)														
Amphoteric														

2.7 Micelles : Structures and Properties

When surfactant molecules are present in aqueous solution at concentrations above their critical micellar concentration (CMC), interactions between the hydrophobic alkyl chains of adjacent molecules provide a force tending to pack them closer to each

other. The hydrophilic head groups, on the other hand, have a strong affinity for water and tend to remain spaced out in the aqueous medium. When the head groups are charged, electrostatic repulsion provides additional force tending to distance the head groups. These opposite forces govern the formation and growth of micelles. The micelles continue to grow until the energy released from the condensation of alkyl chains is balanced by the work done to bring the hydrophilic head groups (which may be charged) into the micellar surface.

The existence of different shapes and sizes of micelles are described [22]. They are also interchangeable from one form to another. These are spherical, cylindrical, flexible- bilayer, planer- bilayer and inverted micelles, depending upon the conditions prevailing in the system. Micelles are not fixed entities but have a transient character. Surfactant molecules rapidly join and leave the molecules, whose aggregation number presents only an average over time.

Stigter [37] introduced a detailed model for ionic micelles. According to this model, the small micelle consists of a spherical hydrocarbon core and an aqueous *Stern layer*. The radius of the micelle is equal to the length of the alkyl tail of the surfactant. The *Stern layer* consists of hydrophilic heads of the surfactant molecules along with a fraction of the counter ions. Outside of the shear surface is the Gouy – Chapman diffuse double layer, which contains an excess of counter ions equal to the charge of the micelle. The model as applied to CPC is shown in Fig. 2.2.

2.8 Selection of Surfactant

In the selection of surfactant for use in MEUF, some important desirable characteristics are [22]:

- [1] high solubilisation capacity for the organic pollutant or adsorption capacity for metal ions
- [2] forms large micelles, so that large pore sizes can be used and
- [3] low monomer concentration, so that little surfactant is wasted

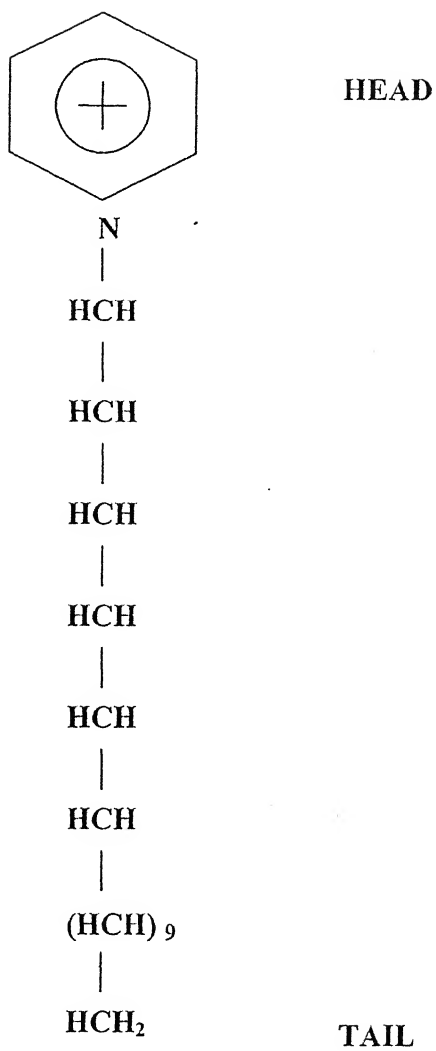
One desirable characteristic of a surfactant is a long hydrocarbon chain, since this result in the formation of larger micelles, high solubilisations and low monomer concentrations.

Nonionic surfactants form large micelles and have low monomer concentrations in micellar solutions. However, the solubilisation or adsorption capacities of the nonionic surfactants are not high compared to anionic or cationic surfactants. Cationic surfactants generally have much lower Krafft temperature than those of anionic surfactants of corresponding hydrophobic group size. Therefore, cationic surfactants with large hydrophobic groups, resulting in large micelles, high solubilisation / adsorption capacities, and low monomer concentrations, may be used in MEUF. Cationic surfactants do not pose significant environmental risks. In general, cationic surfactants are the surfactants of choice in MEUF.

2.9 Recovery of Surfactant

It is important to recover surfactant for reuse in order for the process to be economical. The recovered surfactant will normally be recycled to the process to minimize makeup surfactant requirements.

The process use precipitation of surfactant by using monovalent or multivalent counterions. The surfactant is precipitated from the aqueous solution by addition of an ion of opposite charge to that of the surfactant (the counterion). The precipitate is removed from solution by gravity settling, filtering, or centrifuging. This filter cake is then recycled or further treated if the counterion used for the precipitation is unacceptable in the process. Ultimate recoveries of 95% were shown to be attainable using this process [22].



CETYL PYRIDINIUM CHLORIDE (CPC)

Fig. 2.1 - Structure of CPC monomer

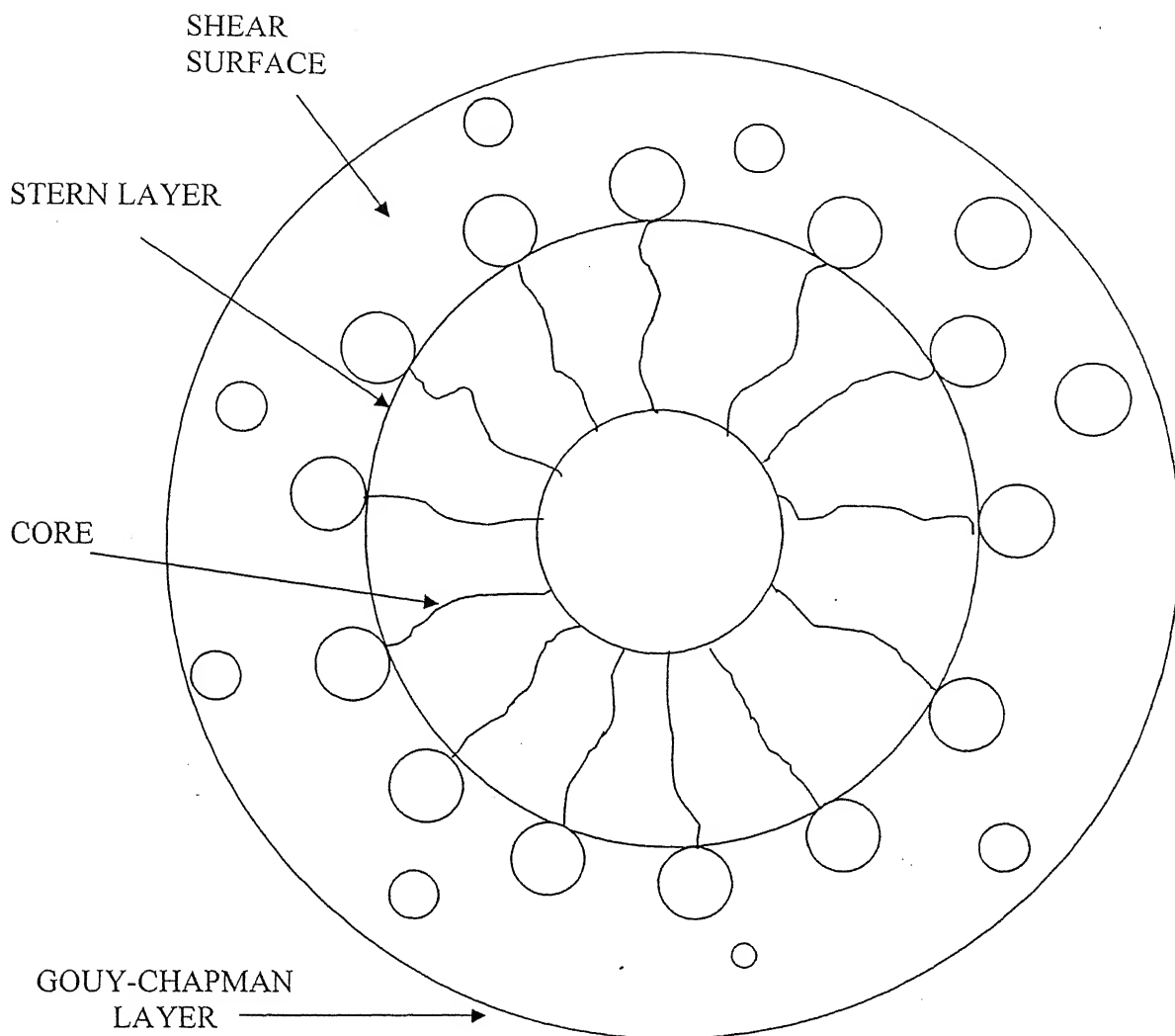


Fig.2.2 - Probable structure of cetyl pyridinium chloride micelle

3.1 Micelle

When surfactants are added to aqueous streams above CMC, they form aggregates of about 50-150 molecules, called micelles. Micelles exist in different shapes and sizes. They are interchangeable from one form to another. Micelles are not fixed entities, but are dynamic in nature. The surfactant molecules rapidly join and leave the micelles, whose aggregation number is only an average over the time.

As described earlier micelle consists of a spherical hydrocarbon core and aqueous Stern layer. A probable structure of micelle is given in the Fig. 2.2. The radius of micelle is approximately equal to the length of the alkyl tail of the surfactant.

3.1.1 Aggregation Number

The number of monomeric surfactant molecules contained in a micelle provides aggregation number. It can be obtained by dividing micellar molecular weight by monomeric molecular weight. Molecular weight of the micelles can be obtained from various techniques including gel filtration, light scattering, sedimentation equilibrium, and small angle X-ray scattering. Aggregation number is influenced by the ionic strength.

$$\frac{\text{micellar molecular weight}}{\text{monomeric molecular weight}} = \text{Aggregation number} \quad (3.1)$$

3.1.2 Concentration of Micelle

CMC may be defined as the lowest concentration above which the monomers cluster together to form micelles. Given CMC, concentration of surfactant and the aggregation number, it is possible to calculate the concentration of micelles in moles/liter using the following equation:

$$\text{Concentration of [micelles]} = \left(\frac{C_0 - \text{CMC}}{N} \right) \quad (3.2)$$

where: N is the aggregation number and C_0 is surfactant concentration

3.1.3 Thermodynamics of Micelle Formation

Two general approaches deal with the micellization. In the first, micellization is regarded as a phase separation, which commences at CMC. CMC is taken to represent the saturation concentration for unaggregated surfactant. In the second approach, micelles and single surfactant ions are considered to be in association – dissociation equilibrium. The CMC in this approach is merely a concentration range above which most of the surfactant appears in micellar form.

Phase Separation Approach

The equilibrium between surfactant ions D^+ , counterions X^- and micelles M is as follows:



The micelle charged aggregate of surfactant ions plus an equivalent of counterions in the surrounding region are treated as a separate phase. The standard free energy of micellization per mole of monomer is given by [38]:

$$\Delta G_{ps}^0 = \frac{-RT}{j} \ln \left(\frac{f_M [M]}{f_D^j f_X^j [D^+]^j [X^-]^j} \right) \quad (3.4)$$

where $[M]$, $[D^+]$ and $[X^-]$ are equilibrium concentrations and f_M , f_D and f_X are the respective activity coefficients.

The standard heat of micellization is [40]:

$$\Delta H_{ps}^0 = -RT^2 \frac{d}{dT} \left[\ln \left(f_D f_X [CMC] [X^-] \right) \right] \quad (3.5)$$

The standard enthalpy of micellization is given by [38]

$$\Delta S_{ps}^0 = \frac{(\Delta H_{ps}^0 - \Delta G_{ps}^0)}{T} \quad (3.6)$$

Mass Action Model

The equilibrium considered here is as follows:



where M^{+z} is thought to be an aggregate of j surfactant ions and $(j-z)$ firmly bound anions. The standard free energy of micellization per mole of monomeric surfactant ions is:

$$\Delta G_{ma}^0 = \frac{-RT}{j} \ln \left(\frac{f_M [M^{+z}]}{f_D^j f_X^{j-z} [D^+]^j [X^-]^{j-z}} \right) \quad (3.8)$$

When j is large, concentrations near [CMC] are used and when there is no added salt, then the above equation changes to:

$$\Delta G_{ma}^0 = \left(2 - \frac{z}{j} \right) RT \ln [CMC] \quad (3.9)$$

if z is zero i.e. j counterions are firmly bound to the micelle so as to give zero charge, the above equation reduces to,

$$\Delta G_{ma}^0 = 2RT [CMC] \quad (3.10)$$

If $z = j$, i.e. no counterions are bound to the micelles then equation (3.14) becomes

$$\Delta G_{ma}^0 = RT \ln [CMC] \quad (3.11)$$

Therefore, the standard heat of micellization is given by,

$$\Delta H_{ma}^0 = - \left(2 - \frac{z}{j} \right) RT^2 \frac{d \ln [CMC]}{dT} \quad (3.12)$$

3.1.4 Mechanism of Micelle Formation

The standard free energy of micellization is known to decrease with increase in chain length [32]. This indicates that with increasing chain length, there is an increase in hydrophobicity of the surfactant. Therefore, the tendency for micelle formation also increases. Further, the tendency of micelle formation is also confirmed by a high positive value of standard entropy of micellization. The explanation for positive entropy values is as follows: alkyl chains induce a structured arrangement of water molecules around themselves. When micellization starts, the alkyl chains aggregate and the structured water molecules revert to ordinary bulk conditions with a considerable increase in entropy.

3.1.5 Properties of mixed micelles

Mixtures of surfactants are often used in many industrial and technological formulations. Because the solution behaviors of these mixed surfactants can be complementary, the resulting synergism often produces properties that are better than those of their individual self-aggregates. Owing to the advantage of mixed surfactants,

the structures and properties of such systems, especially those that are nonionic/ionic, have been extensively studied by various methods. But knowledge of the detailed structure and size of different kinds of mixed surfactant molecules requires further study.

CMC and Interaction Parameter of SDS/TX-100 Mixed Micelles

CMC of mixed surfactant was found by measuring surface tension of SDS/TX-100 mixed surfactant solutions at various mole fractions of SDS [8]. The ideal solution theory on mixed micelles relates the CMC of surfactant mixture (C^*) to the CMC's of pure components (C_i) and the mole fraction of the components (α_i) by

$$1/C^* = \sum_{i=1}^n \alpha_i / C_i \quad (3.13)$$

For non ideal surfactant mixtures, above equation is modified, as below, by considering the activity coefficients of components (f_i) in the mixed micelles.

$$1/C^* = \sum_{i=1}^n \alpha_i / f_i C_i \quad (3.14)$$

3.2 Ultrafiltration

Ultrafiltration refers to separation from the solvent of solute molecules which are at least 10 times bigger than solvent molecules and can be as large as 0.5μ . As the smaller solutes permeate through the membrane, the larger ones are retained. This leads to an accumulation of retained components in the boundary layer adjacent the membrane surface. This phenomenon is referred to as Concentration Polarization. Under certain conditions as the concentration of retained solute increases, large molecular weight solutes may form a 'gel', which precipitates at the membrane surface. Such a precipitate may be in the form of a cake or slimy deposit. It has the undesirable consequence of being a secondary membrane on top of actual UF membrane. The resistance to solvent flow through this cake can be substantial so that the solvent flux is reduced.

3.2.1 Permeate Flux in UF

The permeate flux through the porous membrane can be described by *Darcy's law* for flow through porous media. It states that the volumetric flux is directly proportional to the applied pressure gradient.

$$J = \frac{1}{A} \left(\frac{dV}{dt} \right) = \frac{\Delta P}{\mu_m R_m} \quad (3.15)$$

where R_m is the intrinsic hydraulic resistance of the membrane. It is a function of pore size, tortuosity, membrane thickness, and porosity. R_m is also a function of pressure history. Therefore, membrane needs compaction at a pressure higher than the highest operating pressure.

At low pressure, low feed concentrations and high feed velocity, i.e. under conditions where concentration polarization effects are minimal, the transmembrane pressure will affect flux. However, during UF of macromolecular solutes or at high pressure, the linear relationship between J and ΔP does not hold good because of concentration polarization [41], as modeled below

$$\ln \left[\frac{C_m - C_p}{C_b - C_p} \right] = \frac{J}{k} \quad (3.16)$$

From the concentration polarization model, it may be observed that the concentration of the solute at the membrane surface is considerably higher than that in the bulk. The solute concentration on the upstream side of the membrane being high and on the downstream side being very low creates an osmotic pressure difference ($\Delta\pi$). This acts in opposition to applied pressure. So in equation 3.1 (ΔP) gets replaced by ($\Delta P - \Delta\pi$).

$$J = \frac{\Delta P - \Delta\pi}{\mu_m R_m} \quad (3.17)$$

In some situations, macromolecular solutes may get adsorbed and can foul the membrane and as well can form polarized layer. These phenomenon are incorporated in the above equation by introducing the resistance due to adsorption (R_a) and resistance due to the formation of polarized layer, R_p . Therefore, the equation becomes:

$$J = \frac{\Delta P - \Delta\pi}{\mu_m (R_m + R_a + R_p)} \quad (3.18)$$

3.2.2 Real and Observed Retention

In the membrane separation, the membrane retention for a given solute is usually characterized by the intrinsic or real retention coefficient. This is defined as

$$R_r = 1 - \frac{C_p}{C_m} \quad (3.19)$$

where C_p is the solute concentration in the permeate and C_m is the solute concentration at the membrane surface (retentate side). Since it is difficult to measure C_m experimentally, it is replaced by the bulk retentate concentration C_b , which can be easily measured.

The observed retention coefficient is defined by the following equation:

$$R_o = 1 - \frac{C_p}{C_b} \quad (3.20)$$

However, the observed retention coefficient is not a property of the membrane but depends strongly on experimental conditions under which it is determined.

3.2.3. Sharp cut off UF membrane

A microporous UF membrane in which the width of pore size distribution (PSD) is small, so that the size difference between the solute which is completely retained and the solute which passed through the membrane completely unhindered is small is said to have a *Sharp Cut-off*. A microporous UF membrane, on the other hand, which has a wide size distribution is said to have *Diffuse Cut-off*. The mean pore size distribution will, however, determine the Cut-off level. Fig.3.1 depicts such types of membranes in terms of percent retention of solutes against their sizes (taken by MW).

3.3 Adsorption

When surfactant is added to an aqueous solution containing the target ions at a concentration greater than CMC, the counter ions get adsorbed onto the surface of the micelles formed. Adsorption isotherm is the equilibrium relationship between adsorbed concentration (C_{ads}) and dissolved equilibrium concentration (C_{eq}). The *Langmuir adsorption isotherm equation* is expressed as:

$$C_{ads} = (K_{ad} C_{eq}^n) / (1 + K_{ad} C_{eq}^n) \quad (3.21)$$

Equation 3.21 can be linearised as follows:

$$1/C_{ads} = 1 + 1/(K_{ad} C_{eq}^n) \quad (3.22)$$

where 1 is *Langmuir* constant (μ g/g) and K_{ad} is the *Langmuir* equilibrium constant.

When $n = 1$, *Langmuir* gives rise to linear isotherm.

On the micelle phase boundary (neglecting the *Stern* layer thickness), the metal ion concentration is in equilibrium with the unadsorbed free ion concentration in the bulk phase [9].

3.4 Concentration measurement using UV- VIS spectrophotometer

According to Bouguer – Lambert – Beer (BLB) law, the absorbance at a particular wavelength for a single species is given by

$$A_{\lambda} = a_{\lambda} LC \quad (3.21)$$

where L is the cell path in cm, C is the concentration of the solute in mol l^{-1} and a_{λ} is the molar adsorption coefficient at wavelength λ in $\text{mol}^{-1}\text{cm}^{-1}$. The BLB law is usually valid for dilute solutions, for strongly monochromatic radiation and in optically homogeneous media. It is also valid for a mixture of absorbing species, if there are no mutual interactions, which would contravene the principle of additivity of absorbances.

Let A_1, A_2, \dots, A_n be the absorbances at wavelengths $\lambda_1, \lambda_2, \dots, \lambda_n$ for a sample containing n species. Then for $L = 1$ cm,

$$A_1 = a_{11}C_1 + a_{21}C_2 + \dots + a_{n1}C_n \quad \text{at } \lambda_1$$

$$A_1 = a_{12}C_1 + a_{22}C_2 + \dots + a_{n2}C_n \quad \text{at } \lambda_2$$

:

:

$$A_1 = a_{1n}C_1 + a_{2n}C_2 + \dots + a_{nn}C_n \quad \text{at } \lambda_n \quad (3.22)$$

$a_{11}, a_{21}, \dots, a_{nn}$ may be obtained from the pure component absorbances for the n species at wavelengths $\lambda_1, \lambda_2, \dots, \lambda_n$. A_1, A_2, \dots, A_n are measured using a spectrophotometer.

The equations (3.23) can be solved simultaneously to obtain the concentrations C_1, C_2, \dots, C_n of the n species.

3.5 Cationic surfactant (CPC)

Cetyl pyridinium chloride (CPC) is a cationic surfactant. The apparent constancy of the size of CPC micelles, when compared to other surfactants, makes it ideal for experimental investigations. Anacker [38] determined the aggregation number for CPC in sodium chloride solutions ranging from 0.44 M to 0.73 M and found it to be 136.2. The number is consistent with what one would calculate for a spherical micelle of radius 27.3 and density of ~ 0.9 g/cc. The osmotic pressure for CPC in 0.01 M NaCl solutions was found experimentally by Markels et al [9]. The data was curve fitted and is given by

$$\pi = 0.00366C + 0.01209C^2 - 8.0 \times 10^{-5} C^3 + 2.592 \times 10^{-7} C^4$$

for $C \leq 250$ kg/m³

where π is in kPa and C is the total surfactant concentration in kg/m³. The osmotic pressure at 180 kg/m³, for example, is 210 kPa. Since the applied pressure in Uf is typically 210-1030 kPa, osmotic pressures of this magnitude are clearly significant [41].

The CPC in the permeate was analyzed by UV Spectrophotometer at a wavelength of 259 nm. The calibration curve was prepared for a wide range of the order 1-300 mg/l, (2.87×10^{-3} to 0.84 mM) which is below the CMC (which is 0.88 mM) of the cationic surfactant. The calibration curve is as depicted in the fig. 3.2. The fitting for the calibration curve was obtained to linear.

3.6 Analysis of Arsenic (V) by Molybdenum Blue Method

A relatively simple method is developed, based on the work of Johnson, [42] which allows for routine analysis of arsenite, arsenate, and phosphate by spectrophotometric measurement of the arsenic and phosphate molybdenum blue complexes. The mixed (colour) reagent added to an "untreated" sample produces a colour from molybdoarsenate formed from any arsenate present. In the method here, an oxidizing agent is used to convert arsenite to arsenate; suitable experimental conditions have been established so that the difference between an "oxidized" and a "reduced" sample is the absorbance arising from the total inorganic arsenic. Arsenite is then calculated as the difference between total-As and arsenate that is As (V).

Mixed Reagent: Mix thoroughly 125 ml of 5 N sulphuric acid and 37.5 ml of ammonium molybdate. Add 75 ml of ascorbic acid solution and 12.5 ml of potassium antimonyl tartrate solution. This reagent should be prepared as required as it should not be kept for more than 24 h [43].

Standards: Stock solutions of arsenate having final concentration of 1-2 mM from reagent-grade sodium arsenate were prepared. Appropriate dilutions were done to prepare fresh working standards. Calibration of the method is conveniently made by means of standard additions in the 0.5-1.0 μM range as shown in the fig. 3.3, 3.4 and 3.5.

Procedure: Pipette out 40 ml of sample ("untreated sample" containing only As-V) into a 50 ml calibrated flask (glass stoppered tests tubes), add 4 ml of the freshly prepared mixed reagent to it and shake vigorously. Add 2 drops of the 50% saturated potassium iodate solution. Mix well after each addition. Then add 1 ml of 1 M hydrochloric acid to each of the diluted permeate sample of As-V ("untreated sample"). Allow the colour formation by keeping it in a water bath for 2 h. Then the absorbance was read in the UV-Spectrophotometer in a 10-cm cell at a wavelength of 865 nm corresponding to which the unknown concentration of the permeate sample was read.

For the determination of As-III, first the samples were oxidized ("oxidized" sample) by adding 1 ml of HCl and 2 drops of 50 % saturated potassium iodate. The oxidation was allowed to take place for 2 minutes. Then 4ml of mixed reagent was added followed by the addition of 1 ml of 1 M hydrochloric acid and then 2 drops of the 50% saturated potassium iodate solution. Since the arsenite concentrations are calculated from the difference in absorbance (oxidized minus untreated), a negative arsenite value can be obtained when the arsenite levels are low (less than about 0.1 μM). To avoid this difficulty oxidizing reagent is added to the "untreated" sample aliquots also after the addition of mixed reagent.

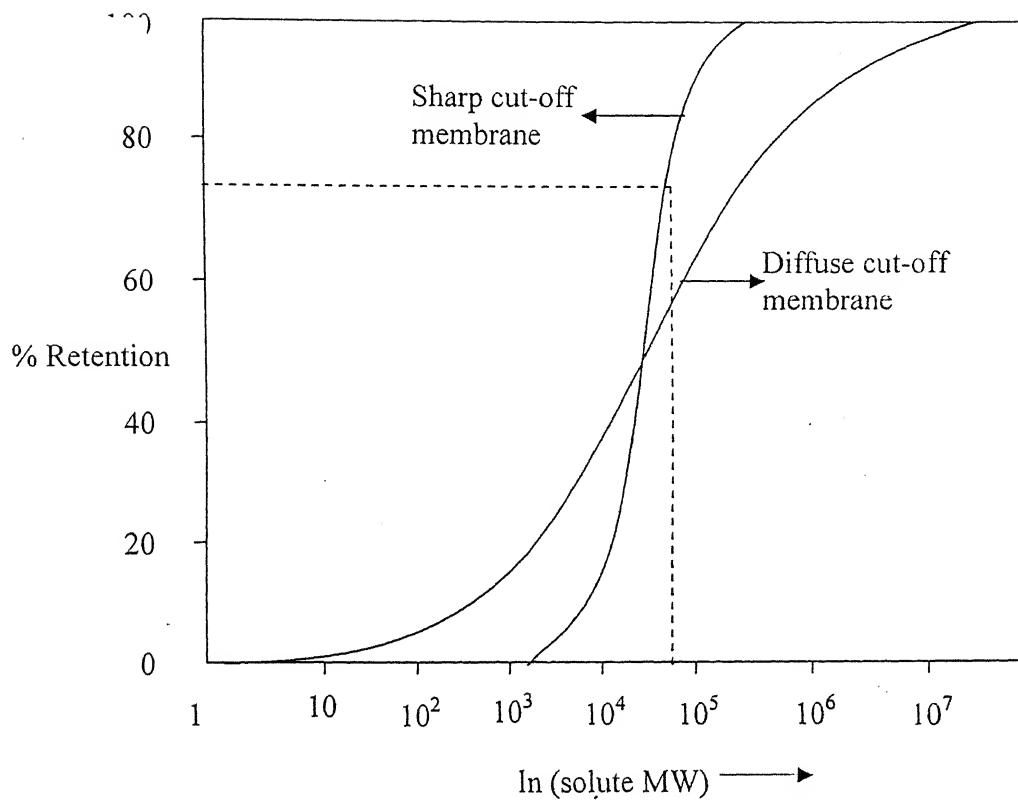


Fig. 3.1 - Percent retention vs. $\ln(\text{solute MW})$

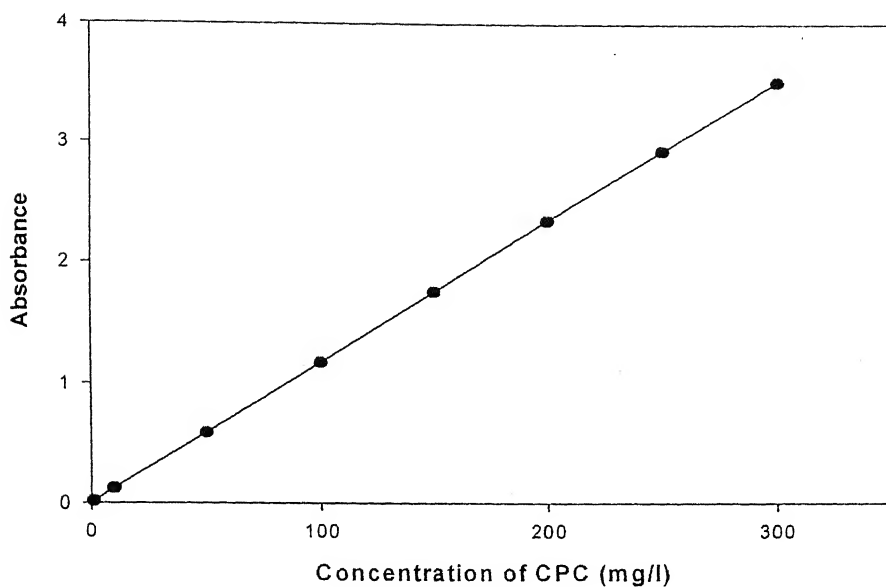


Fig. 3.2 - Calibration curve for CPC concentration measurement

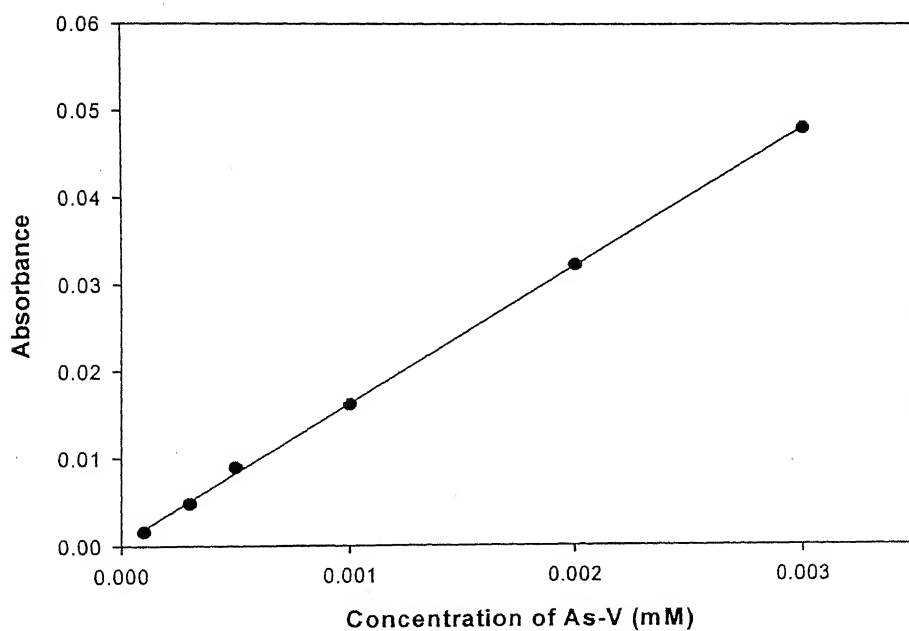


Fig. 3.3 - Calibration curve for As (V) concentration measurement in the range of - 0.0001 to 0.003

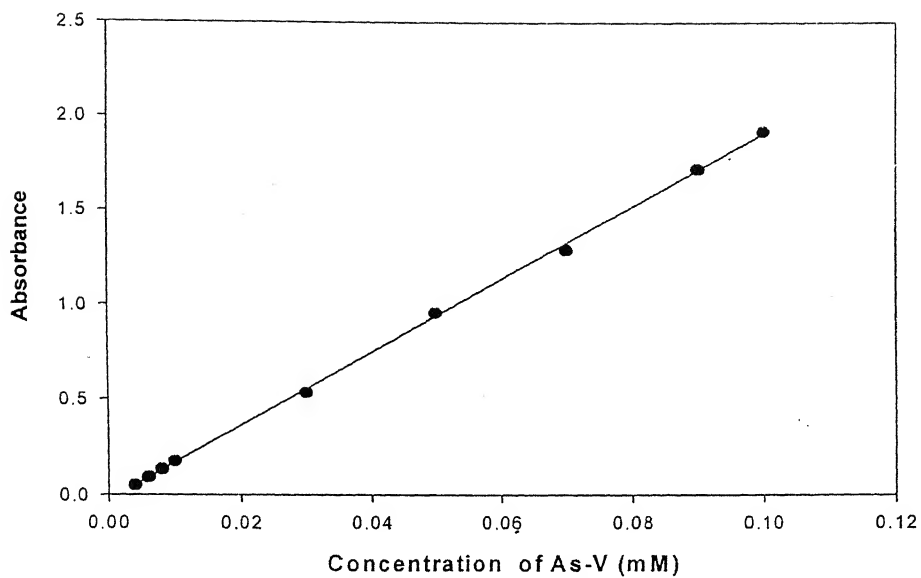


Fig. 3.4 - Calibration curve for As (V) concentration measurement in the range of - 0.004 to 0.1

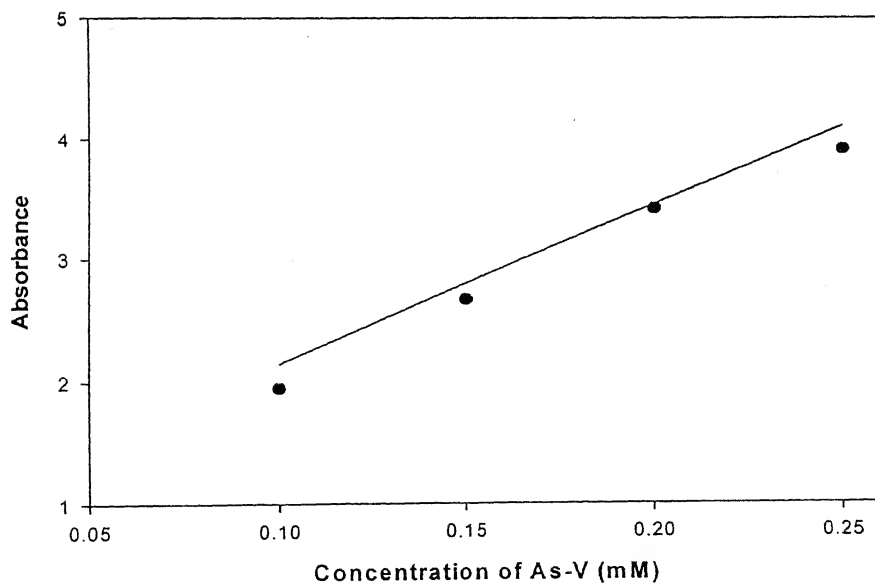


Fig 3.5 - Calibration curve for As (V) concentration measurement in the range of - 0.01 to 0.25

4.1 Membrane and Chemicals

Membrane

Type, Polymer material	: GR81PP; Polysulphone
Company	: Danish Separation Systems, Denmark
Diameter of Flat sheet	: 76 mm
Effective Diameter	: 67 mm
MWCO	: 10,000
Temperature, pH, Pressure Range	: 0 -75°C, 1 – 13, 0 – 145 psi

Chemicals

- Sodium Chloride of purity 99.9% was procured from BDH, Mumbai.
- Cetyl Pyridinium Chloride [$C_{21}H_{38}ClN$] of purity 98% was obtained from Loba Chemie, Mumbai.
- Sodium Arsenate of purity 98.5.0% was procured from Loba Chemie, Mumbai.
- Arsenic trioxide Pract of purity 95% was procured from S.D.Fine-Chem Ltd., Mumbai.
- L-Ascorbic acid LR of purity 99% was procured from S.D.Fine-Chem Ltd., Mumbai.
- Antimonyl Potassium Tartrate of purity 98% was procured from Burgoyne Reagents, Mumbai.
- Potassium Iodate of purity 99.9% was procured from Qualigens, Mumbai.
- Ammonium Molybdate AR of purity 99% was procured from Samir Tech-Chem Pvt. Ltd., Gujarat.
- Nitric acid of purity 69.7% was procured from Qualigens, Mumbai.
- Sulphuric Acid of purity 97-99% was procured from Qualigens, Mumbai.
- Hydrochloric Acid of purity 37.37% was procured from Qualigens, Mumbai.
- Formic acid of purity 98% was procured from Qualigens, Mumbai.

4.2 Instruments and other auxiliaries

UF Cell Specification

UF cell was designed and manufactured at the workshop in IIT, Kanpur.

Material of Construction	: SS – 316
Total useful volume	: 300 ml
Residual Volume	: 100ml
Maximum Operating Pressure	: 1000 kPa

Weighing Balance

Model	: Afcoset Electronic Balance
Accuracy	: 0.0001 g
Maximum Weight	: 180 g

VIS – UV Spectrophotometer

Model ,Type	: UV – 1601, Double beam,
Company	: Shimadzu Corporation, Japan
Wavelength range	: 190-1100 nm.

Mechanical Shaker

Model	: SW-23 (Julabo-Germany)
Temperature range,	: ambient to 90°C.
Rpm range	: 0-220 (Liquid circulation possible)

4.3 Solutions

Solutions of cetyl pyridinium chloride and Sodium arsenate were prepared with 0.01 M sodium chloride in distilled water. The presence of salt decreases the CMC of ionic surfactants and thereby, reduces the loss of surfactant in the monomeric state.

4.4 Measurement of Density and Viscosity

The density of solutions was measured using specific gravity bottle at the ambient temperature. The viscosity was measured using an Ostwald viscometer at ambient temperature.

4.5 Design of Experiments

Experiments were designed to study the effects of As^{+5} feed concentration, operating pressure, cationic surfactant (CPC) feed concentration on the flux and percent removal of arsenic from the stream. The flux and the removal through adsorption of arsenate (pentavalent arsenic) on the surface of the micelles (formed by CPC cationic surfactant) were studied for a wide range of arsenic feed concentrations (between 0.01 to 14 mM). Further, CPC concentrations were varied in the range of 2 to 240 mM for observing the effective % removal of arsenic.

Exclusive arsenic runs were also taken to observe the % removal and flux characteristics in the absence of cationic surfactant; however, all the runs were taken at a pressure of 689 kPa. In an exclusive run of 0.1 mM pentavalent arsenic (made by sodium arsenate) permeate flux and the % removal of arsenic was studied as a function of time at three different pressures: 413, 551, 689 kPa.

4.6 Experimental Procedure

4.6.1 Estimation of Hydraulic membrane resistance

A batch mode UF cell was utilized for experimentations. A fresh membrane was placed on the porous support, as shown in the Fig.4.1. The cell was then assembled and filled with distilled water for initial compaction of the membrane. For this purpose, the cell was pressurized using an air compressor and the flux was measured as a function of time. The operation was carried out for six hours at a pressure of 896 kPa, higher than highest operating pressure to ensure no further compaction during the actual experimentations. Constancy of water flux during this period suggested necessity of negligible further compaction. The pressure was then varied and the flux was recorded as

a function of applied pressure. Simple Darcy's law (refer equation 3.15) was utilized for the estimation of R_m ; accordingly, the hydraulic membrane resistance was obtained from the linear relationship of pressure vs. flux data. Further, to calculate flux, cumulative volume of water was collected in measuring cylinder and time for the collection was noted.

4.6.2 Procedure for MEUF experimental run in batch Mode

After estimation of R_m the cell was dismantled and the membrane was rinsed with distilled water, in order to remove traces of impurities that might have deposited over membrane surface through piping, fittings and joints. For experimental runs, the test solution was poured into the cell. It was pressurized and the permeate flux was measured at regular intervals. Further, samples were collected to measure permeate concentrations. Surfactant concentration was measured directly from VIS – UV spectrophotometer at a wavelength of 259 nm. Concentration of arsenate (in pentavalent form) in permeate was measured by first treating the permeate with the methylene blue method (section 3.7) and then reading the absorbance values using VIS – UV spectrophotometer at the wavelength of 865 nm.

After each run, the cell was rinsed with distilled water. The membrane was washed thoroughly and rinsed with distilled water. The water flux was measured after each run to check the loss of permeability of the membrane in terms of measuring R_m .

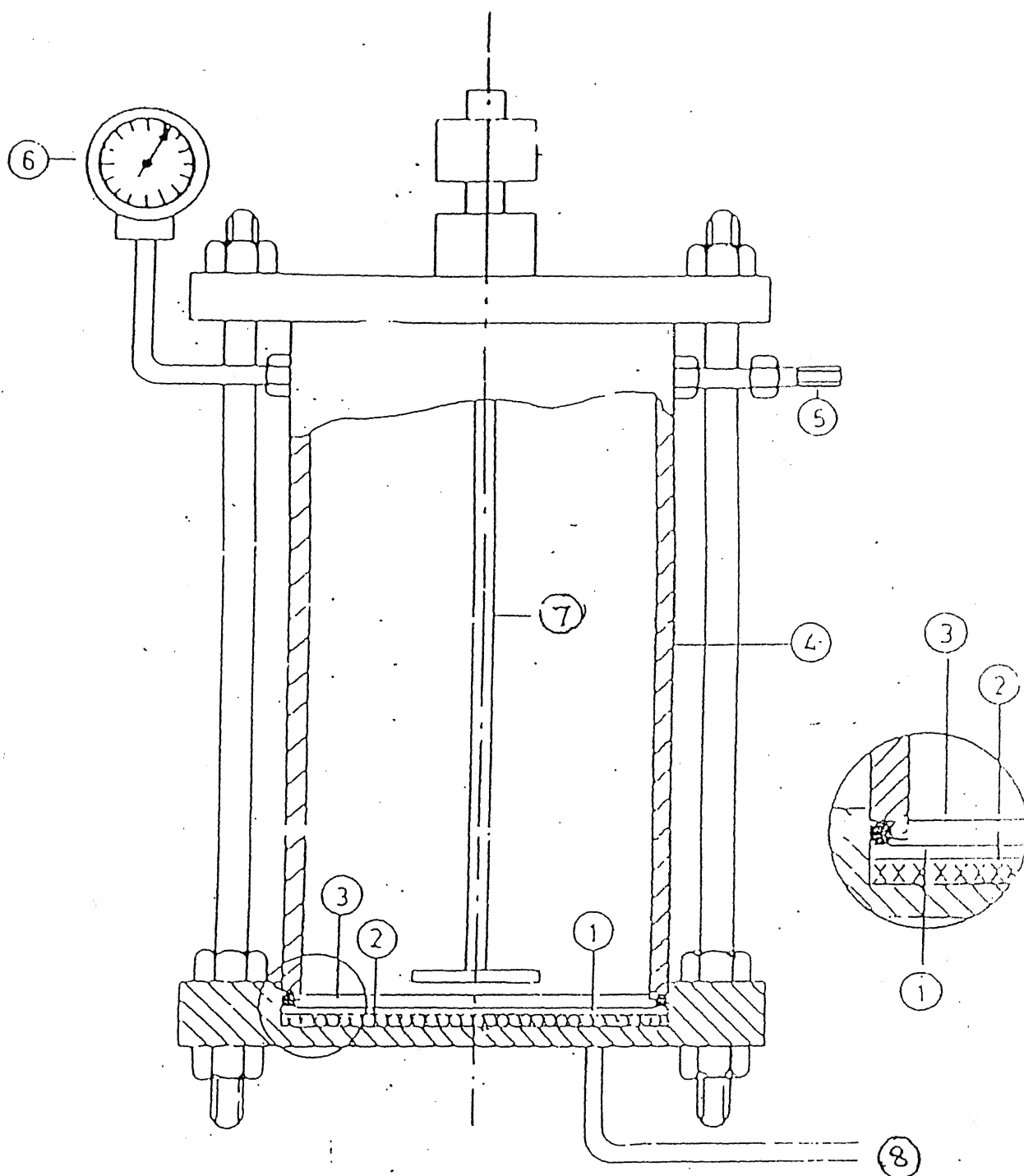


Fig. 4.1 Ultrafiltration Cell

1. Membrane 2. Porous Support 3. 'O' Ring 4. Cell Body 5. Pressure line Connector 6. Pressure Gauge 7. Stirrer 8. Sample Outlet

Micellar enhanced ultrafiltration studies were conducted for the removal of arsenic in pentavalent form (anionic ions) from aqueous solution. The objective is to specifically study the effects of operating conditions, such as concentration of both CPC & arsenate and operating pressure the permeate flux, surfactant rejection and arsenate removal.

5.1 Selection of operating conditions

According to osmotic pressure model (refer equation 3.15) flux depends on the difference between the applied pressure and the osmotic pressure. However, osmotic pressure is negligible in case of CPC, as the micelles formed are of considerable size. A concentration, as high as 180 kg/m^3 of CPC, the solution exerts osmotic pressure of around 210 kPa [9] which is low as compared to many other low MW solutes. To obtain flux at measurable level, the operating pressure range was kept on the higher side and was varied from 413 to 689 kPa.

The micelles of CPC are formed at a critical micellar concentration (CMC) of 0.88 mM. Since, number and size of the micelles depend upon the feed surfactant concentration, the concentration of feed CPC was varied from 2-240 mM. This was done in order to study the behavior of removal of As (V) adsorbed on the micelle surface over CMC of CPC. The feed concentration of As (V) was varied from 0.01 mM to 14 mM. Blank runs with As (V) and As (III) were also taken at varying pressures for a fixed arsenate concentration.

Pentavalent arsenic remains in solution as HAsO_4^{2-} and H_2AsO_4^- in the pH range of 6.77-11.3. All the feed solutions were nearly having the pH in between 7-8. Hence, anionic surfactant could not be used for the present case. The solubilization as well as the adsorption capacities of the nonionic surfactants is not high compared to ionic surfactants. Accordingly, it was decided to carry out experiments with cationic surfactants which in fact further provided advantages in terms of low Krafft temperature

and possibility of the formation of larger micelles. Therefore cetyl pyridinium chloride, a cationic surfactant, was used as it has a large hydrophobic group with the Krafft temperature of 10.8 °C. This property of it enabled us to use effectively at room temperature.

5.2 Ultrafiltration of arsenic in the absence of surfactant

It was thought appropriate to observe the behavior of arsenic solution with out surfactant during UF in terms of observing percent retention as well as permeate flux. These are also called as the blank runs. For this, experiments were conducted in batch mode in unstirred pattern. Before conducting experiment, membrane was saturated with arsenate solution by keeping the membrane in As (V) solution for a longer period of time. Fig 5.1 and Fig. 5.2 show the permeate flux and the percent retention of arsenic, respectively as a function of time at three different pressures for an arsenic concentration of 0.1 mM. Although negligible effect of concentration polarization is observed, there is a clear evidence of it with respect to increase in pressure as observed from Fig.5.1; particularly during the initial period of ultrafiltration. Likewise, from Fig.5.2, it is evident that there is a distinct drop in percent retention during the initial period. This is because of initial adsorption of arsenic with the polymeric membrane. In the initial period of experiment, maximum retention is observed and as time progressed, it reaches a very small value.

However, the retention of As (V) was found to be more as compared to the retention of As (III) at the same pH of 7.5, which is depicted in the Fig. 5.4. This is because, as depicted earlier in the table the arsenite [As (III)] exists in the form of H_3AsO_3 (neutral molecule) and arsenate [As(V)] exists as H_2AsO_4^- and HAsO_4^{2-} (anionic solute) in the pH range of 5-8 [20].

Fig. 5.5 represents the variation of percent retention of pentavalent arsenic and permeating flux as a function of applied pressure for an initial arsenate concentration of 31.2 ppm (0.1 mM). The plot shows that the retention of As (V) in water decreases from 6.75 to 4.95 % with the increase in pressure from 413 to 689 kPa. Such a low retention value suggests that there may be little adsorption of arsenate on the membrane surface

while most of it permeates through the membrane. The permeate flux is found to vary linearly with pressure, indicating insignificant development of resistance against flow at such a low value of arsenate concentration in feed.

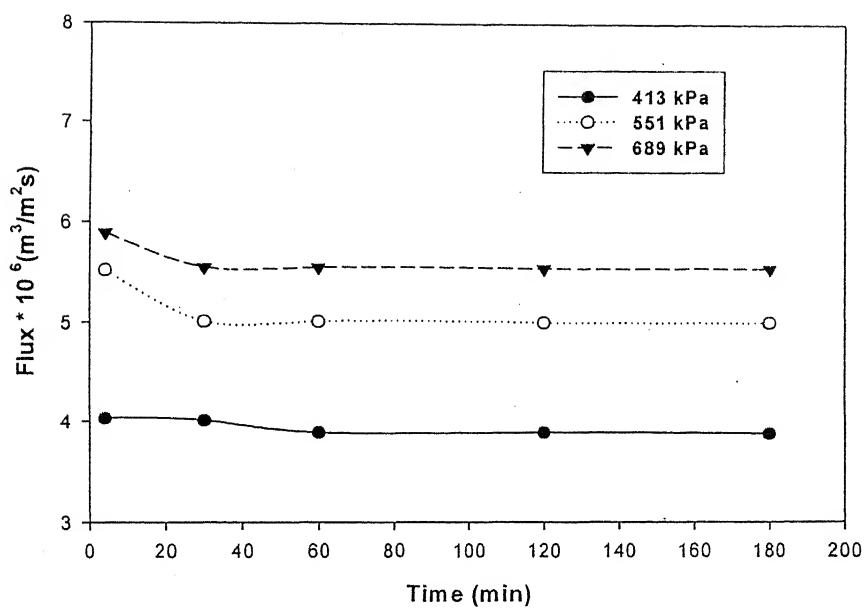


Fig. 5.1 - Flux data for exclusive runs of As (V):0.1 mM at different pressures

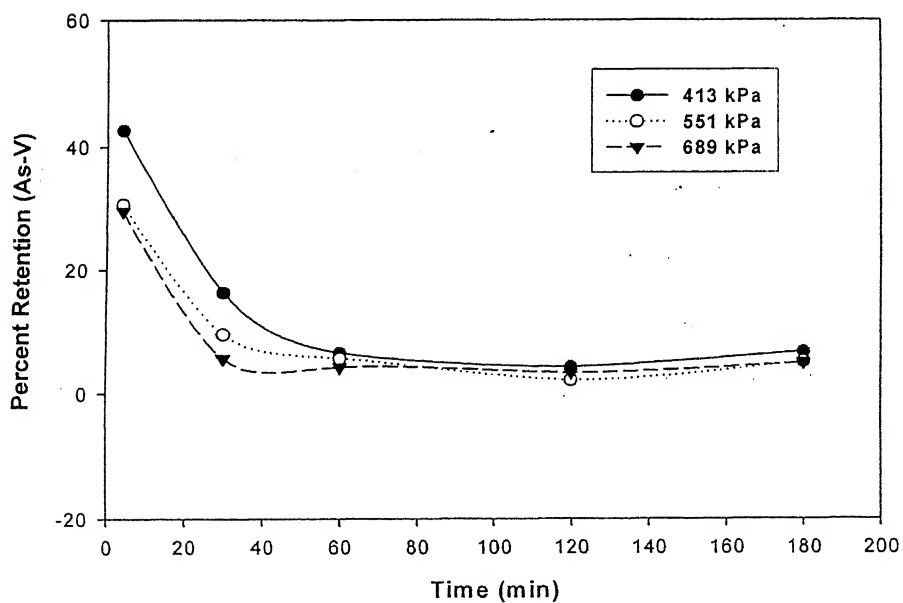


Fig. 5.2 - Retention data for exclusive runs of As (V): 0.1 mM at different pressures

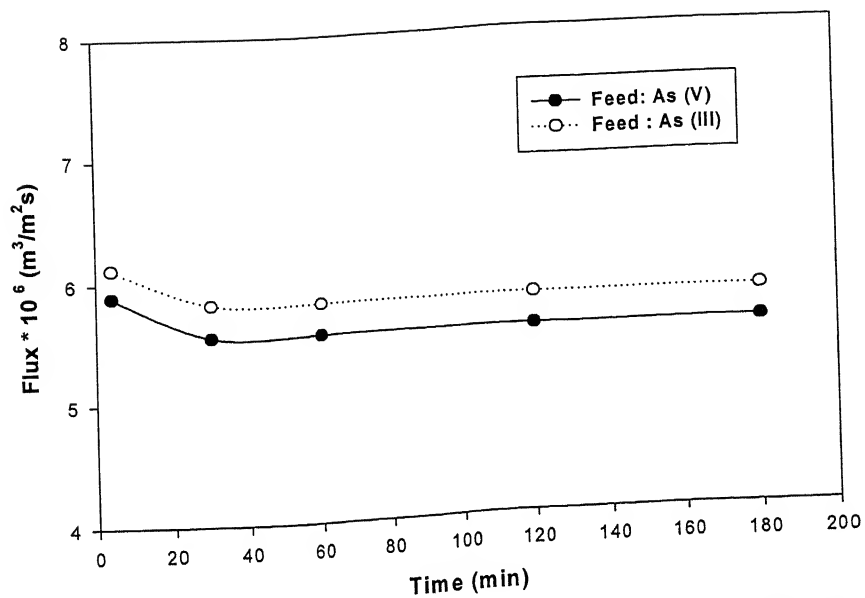


Fig. 5.3 - Flux data for As (V) vs. As (III) (0.1 mM) at 689 kPa

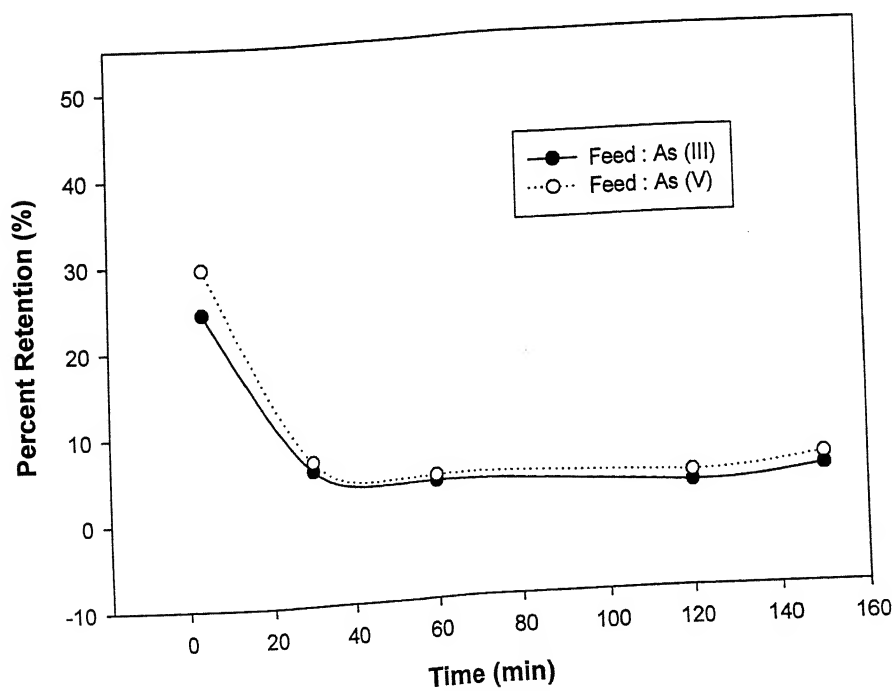


Fig. 5.4 - Percent retention data for As (V) vs. As (III) (0.1 mM) at 689 kPa

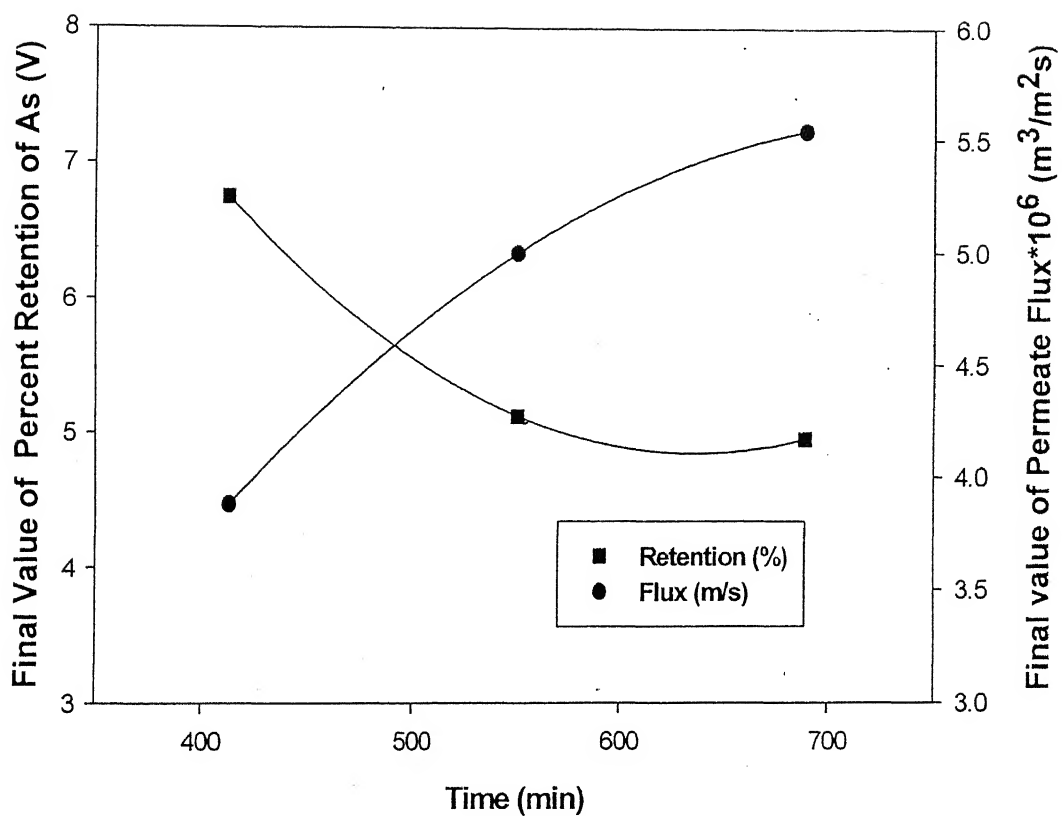


Fig. 5.5 - Percent retention & permeate flux of arsenate solution of 0.1 mM (31.2 ppm) as a function of applied pressure

5.3 Separation of arsenate [As (V)] using surfactant solution

The experiments were carried out with the surfactant and the metal ion. These are called the micellar runs. The solutions containing both of them were prepared for UF. The pH of the solutions was found to be in the range of 6.5-7.5 for all the concentration of arsenate ions in the CPC solution. It is known that at this condition of pH, the arsenate [As (V)] ions mostly exists in the form of HAsO_4^{2-} in the solution. The effects of feed surfactant concentration and metal ion concentration were studied, which included the effects of pressure on permeate flux and arsenate adsorption on the micelles (measured in terms of retention during UF). Basically, the study takes care of the variation in the nature of flux and removal of arsenate adsorbed on the micelle surface over a wide range of arsenate concentrations. The concentration of As (V) was varied from 0.01 mM to 14 mM; for which the concentration of CPC was varied from 2-240 mM (all were above the critical micellar concentration of CPC).

5.3.1 Effect of surfactant concentration

The effects of concentration of CPC were studied for a wide range of arsenate concentrations. The flux and percent retention data were analyzed for very high as well as very low arsenate concentrations. The concentrations were varied from 0.01-14 mM and the CPC concentration was varied (adjusting to obtain around 99% retention of arsenate).

As expected and interestingly, there was no variation of flux with time as shown in Fig.5.6, 5.8, 5.10, 5.12, 5.14. This suggests complete absence of pore plugging due to adsorption of arsenate ion on the membrane surface. It also shows the negligible influence of concentration polarization, as the permeate flux was observed to be invariant with time in presence of arsenate ions for all concentration values of CPC. The decline is marginal in the lower concentration range. However, with the increase in surfactant feed concentrations, larger fraction of micelles are formed. Such larger portions of micelles may form an aggregation layer and may be called micellar aggregation layer (MAL). Hence, the MAL thickness may increase; as a result the resistance offered by this may also increase, consequently declining permeate flux with the increase of feed surfactant concentration.

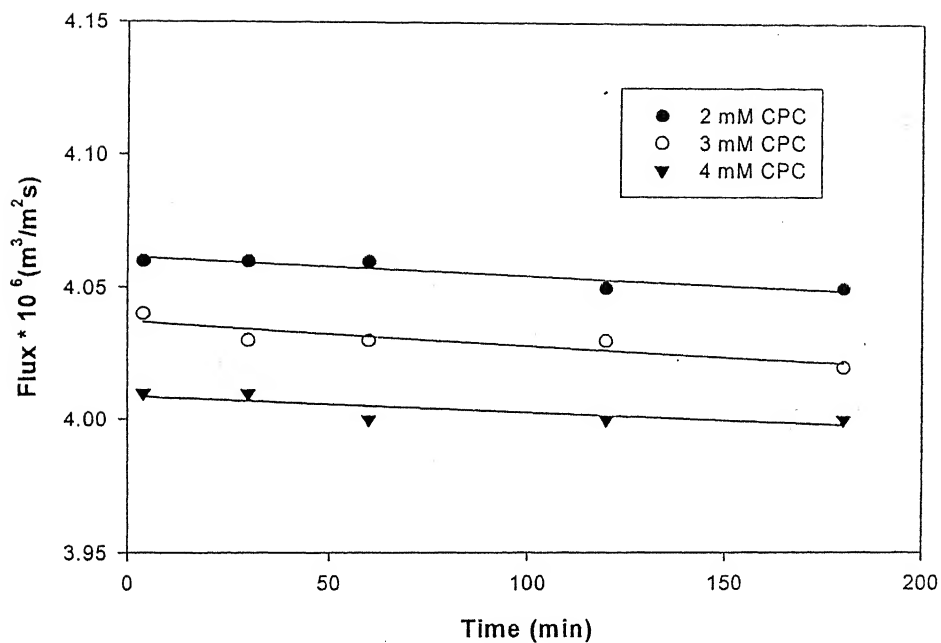


Fig. 5.6 - Flux data for 0.01 mM As (V) at 689 kPa at different CPC concentration

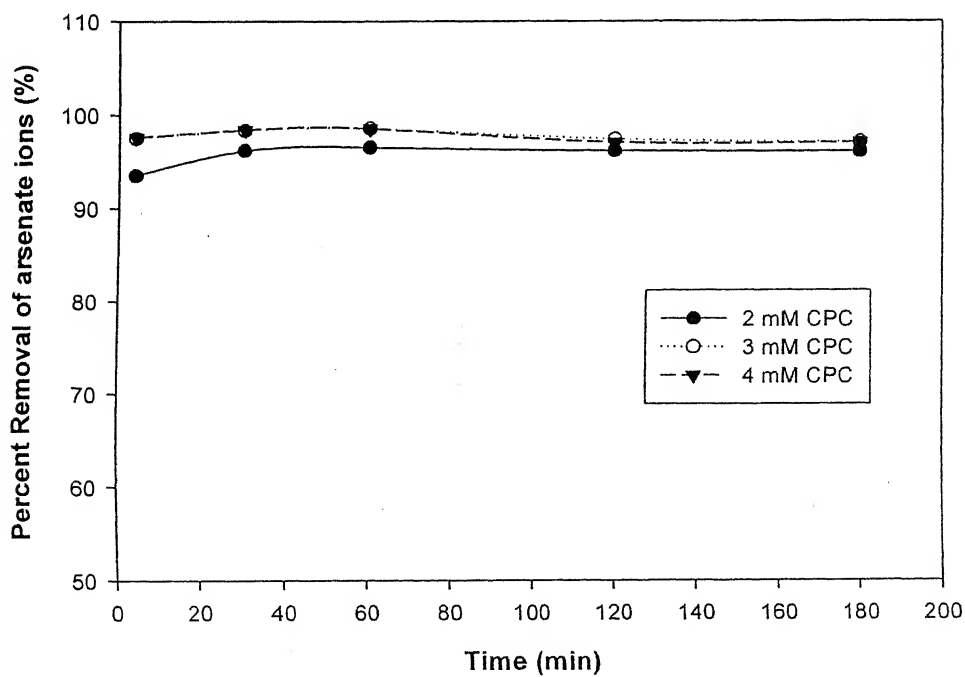


Fig. 5.7 - Variation of percent retention with time at As (V) = 0.01 mM & 689 kPa

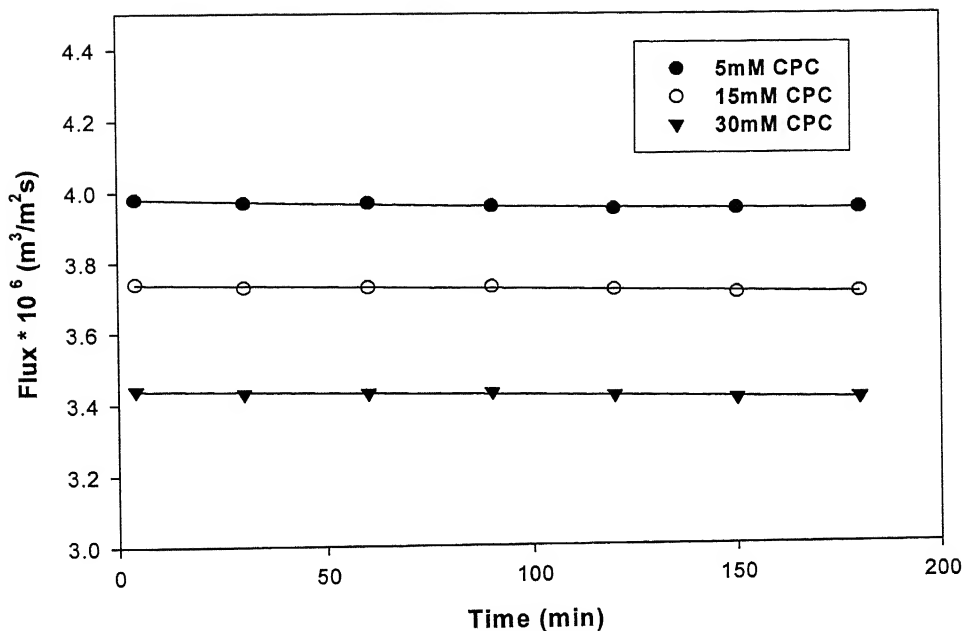


Fig. 5.8 - Flux data for 0.1 mM As (V) at 689 kPa at different CPC concentration

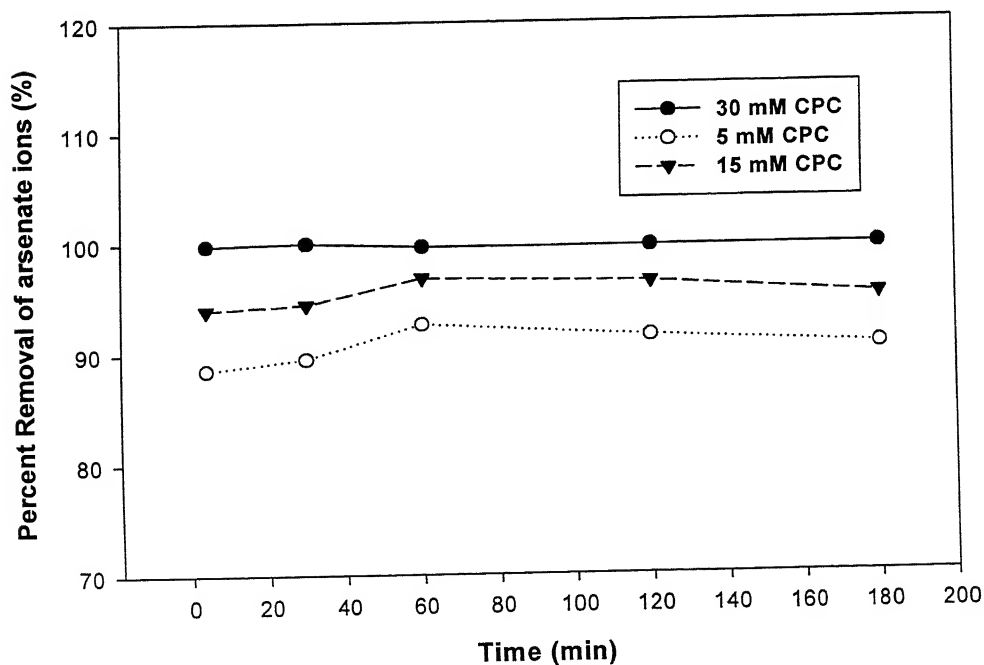


Fig. 5.9 - Variation of percent retention with time at As (V) = 0.1 mM & 689 kPa

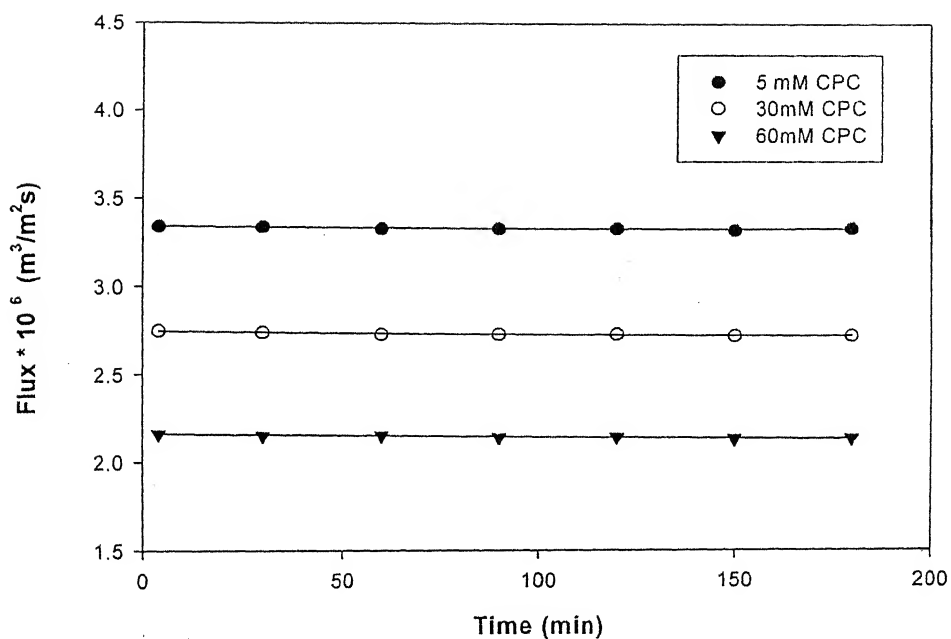


Fig. 5.10 - Flux data for 1 mM As (V) at 689 kPa at different CPC concentration

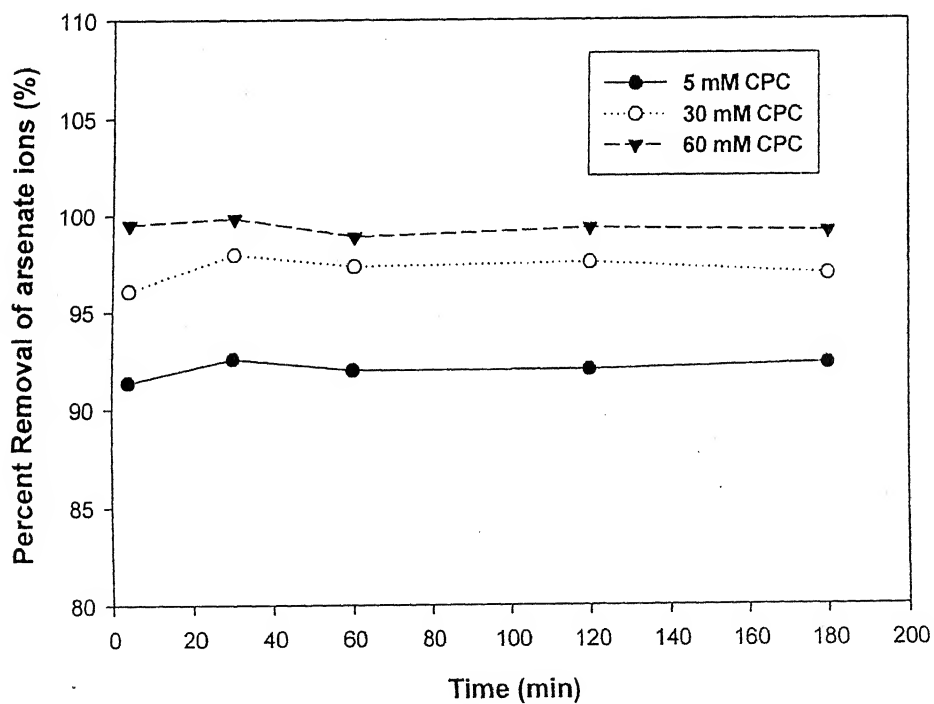


Fig. 5.11 - Variation of percent retention with time at As (V) = 1 mM & 689 kPa

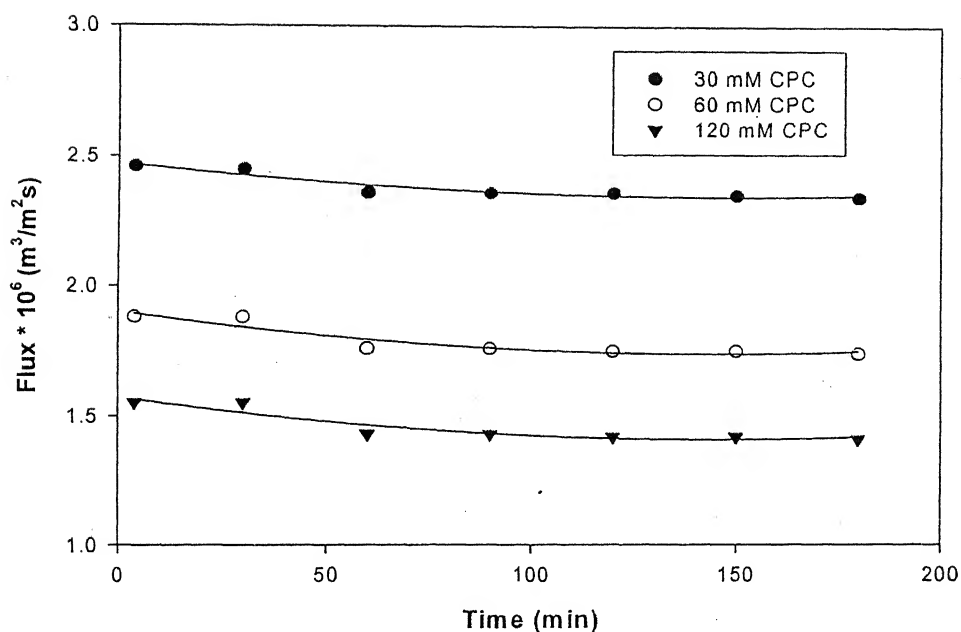


Fig. 5.12 - Flux data for 5 mM As (V) at 689 kPa at different CPC concentration

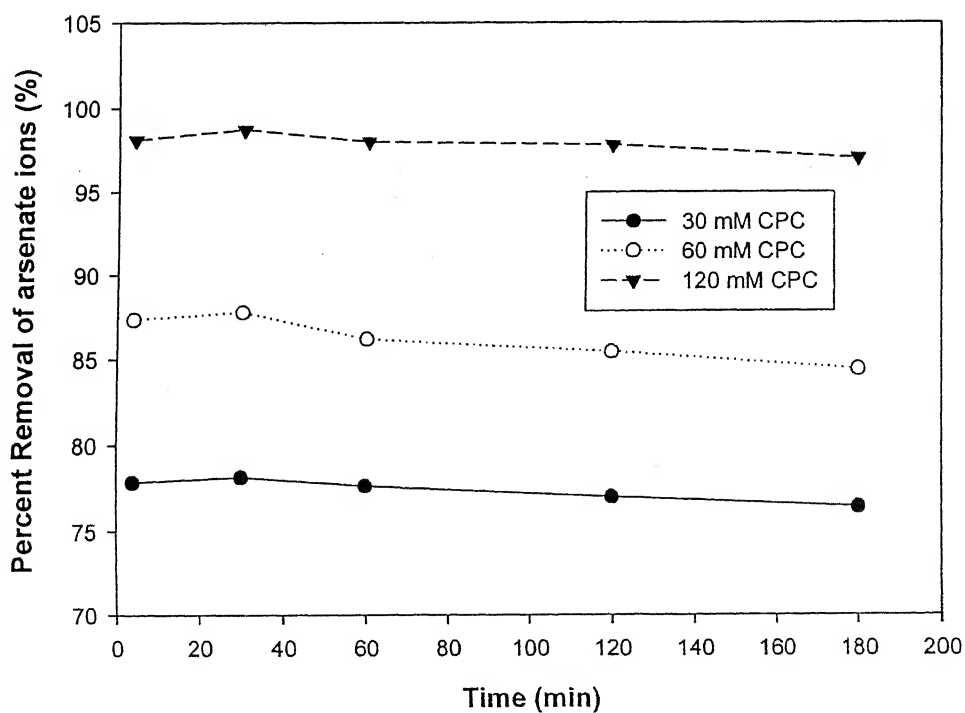


Fig. 5.13 - Variation of percent retention with time at As (V) = 5 mM & 689 kPa

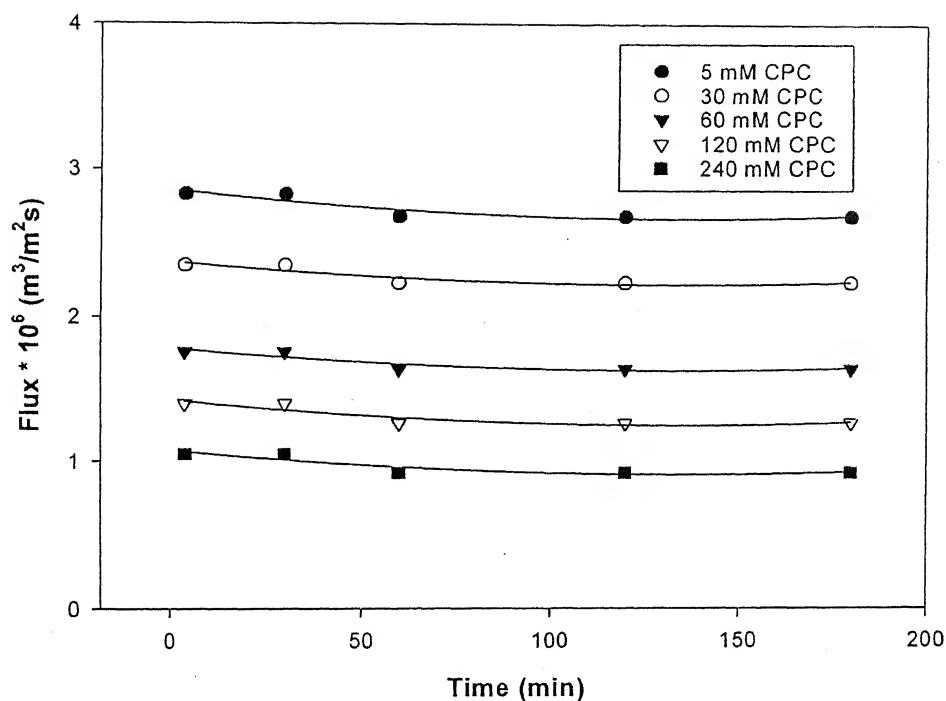


Fig. 5.14 - Flux data for 14 mM As (V) at 689 kPa at different CPC concentration

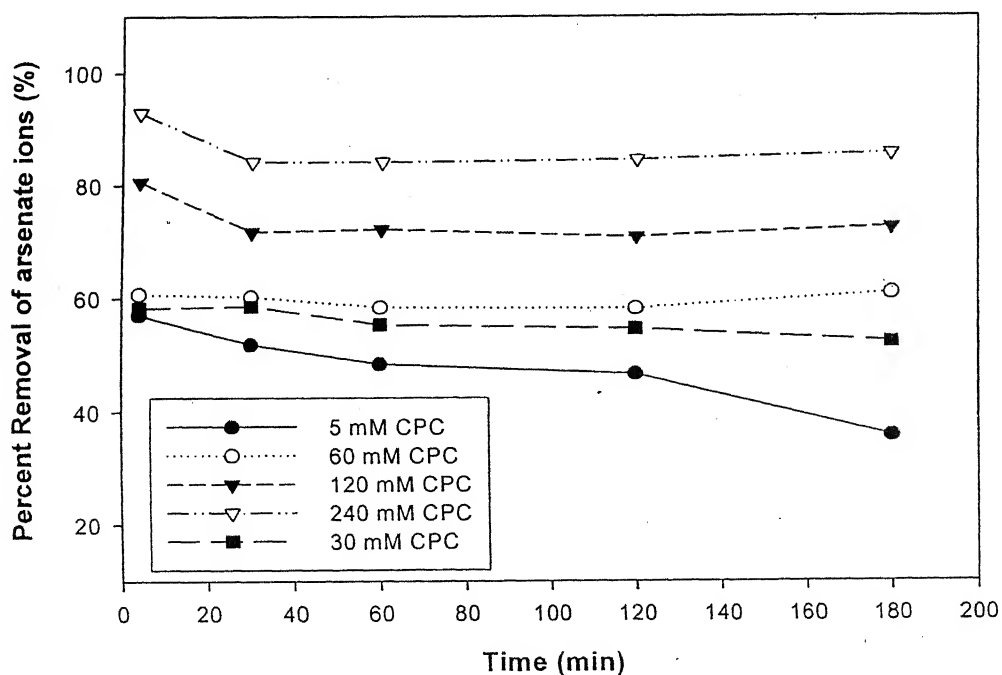


Fig. 5.15 - Variation of percent retention with time at As (V) = 14 mM & 689 kPa

The reduction in permeate flux may be also due to the partial coverage of the membrane pores by these micelles and this effect increases with the increase in feed concentration.

The removal patterns are however different for different arsenate concentrations. Fig 5.7 shows percent removal for very low arsenate concentration of the order 0.01 mM. There is a very marginal increase in retention for 4 mM CPC concentration; after which it declines and become less than the percentage retention obtained by 3 mM CPC solution. This small variation may be either due to the experimental error or because of the fact that beyond a certain CPC concentration the adsorption capacity of arsenate becomes more or less same. Thus, percent removal remains same. In other words, with increase in surfactant concentration the mole fraction of micelles also increases. Accordingly, larger adsorbing sites could have become available for the arsenate; however, such larger micelles keep forming and breaking which therefore may saturate adsorption of arsenate per unit mass of micelles beyond an increase in the concentration of surfactant.

For the concentration of 0.1 mM and 1 mM arsenate as observed in the Fig.5.9, Fig. 5.11, there is an initial increase in the percentage removal and then saturation was observed (as time proceeds). This was common observation for all CPC concentrations taken for that specific arsenate concentration. This may be due the fact that with the increase in CPC concentration the mole fraction of micelles increases and as a result the adsorption of arsenate on the micelle surface increases. However, again, once a very high adsorption is achieved under complete formation of micelles that the retention becomes almost constant because of dynamic formation and breaking of micelles. Further, as shown in Fig.5.11, percent removal of arsenate is beyond 99.0 as the concentration of CPC is increased to 60 mM. Fig. 5.13 shows the variation of % removal of arsenate at 5 mM As (V) feed concentration. Here also the % removal increases with time (upto the 20th minute of the experimental run). If at all there were any fall in percent removal, as somewhat observed, that may be due to coupling between broken small size micelles and arsenate ions that might be permeating through the 10,000 MWCO membrane used for the purpose. Fig. 5.15 shows the pattern of percentage retention at very high arsenate concentration (14 mM). A perceptible decrease in retention is seen at the initial period

after which more or less it remains constant. This may be due to the fact that adsorption may not be favored at this high concentration of arsenic as percent removals were obtained around 99 with other lower concentrations of arsenic. Also, there may not be enough adsorption sites available (with a maximum of 240 mM CPC) due to which most of the arsenates pass through the membrane. Further, at such a high concentration of arsenic the rate of adsorption may also be small which is evidenced through a significant decrease in the removal value of arsenate ions in the initial period. It may also be inferred that the higher concentration of arsenate in water is affecting the stability of micelle, which in turn is reducing the amount of adsorption of the arsenates on the micelle surface.

Fig 5.16 shows the variation of final values of percentage retentions of 14 mM As (V) run as a function of CPC concentration. From the graph it is observed that the % removal of As (V) increases with increase in CPC concentration and then it attains a plateau. As feed concentration increases there is a possibility of the formation of micellar aggregation layer (MAL) which would pose additional resistance to the flux and lead to a decline in the removal rates of As (V).

5.3.2 Effect of arsenate concentration

Fig. 5.17 shows the permeate flux at varying arsenate concentrations for a constant surfactant concentration of 30 mM. As inferred from the graph the permeate flux more or less remains constant over the time range, indicating concentration polarization to be negligible. However, on close observation there is an evidence of linear decline in flux. The decline is so little that a trend with arsenate concentration could not be observed.

Fig. 5.18 shows the influence of arsenate concentration on final values of flux. It is observed that with the increase in arsenate concentration there is a distinct decrease in permeate flux. It is evident that at higher arsenate concentration the decline in flux is comparatively less. It was stated [34] that this might be due to the formation of mixed micelles. Arsenate ion replaces the chloride ions from the micelles. With the increase in the metal ion concentration, the fraction of micelles containing arsenate ions increases.

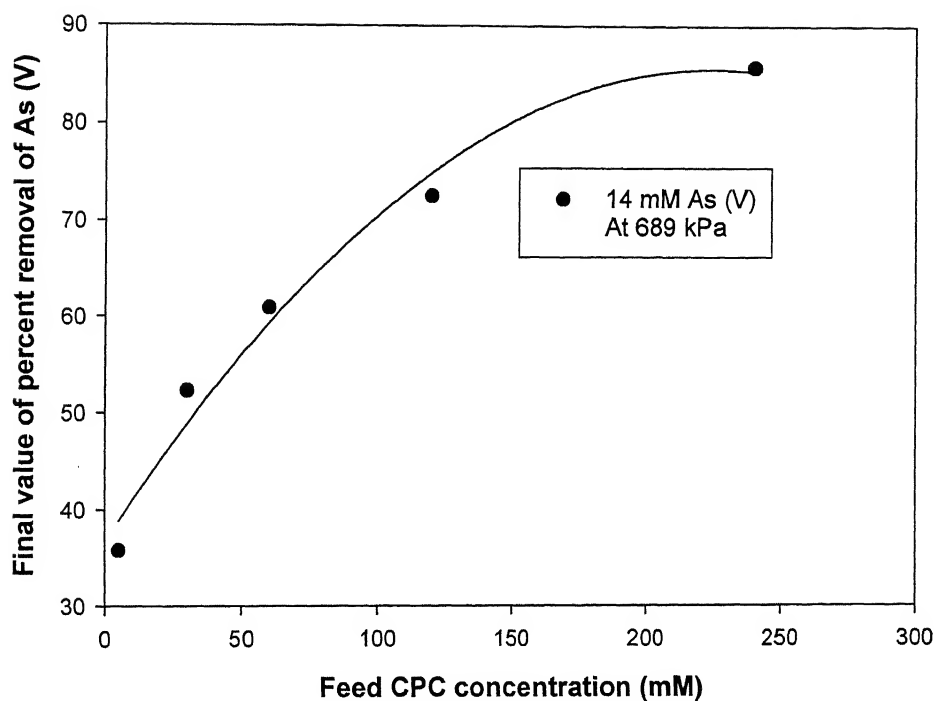


Fig. 5.16 Final value of Percent removal as a function of feed CPC concentration

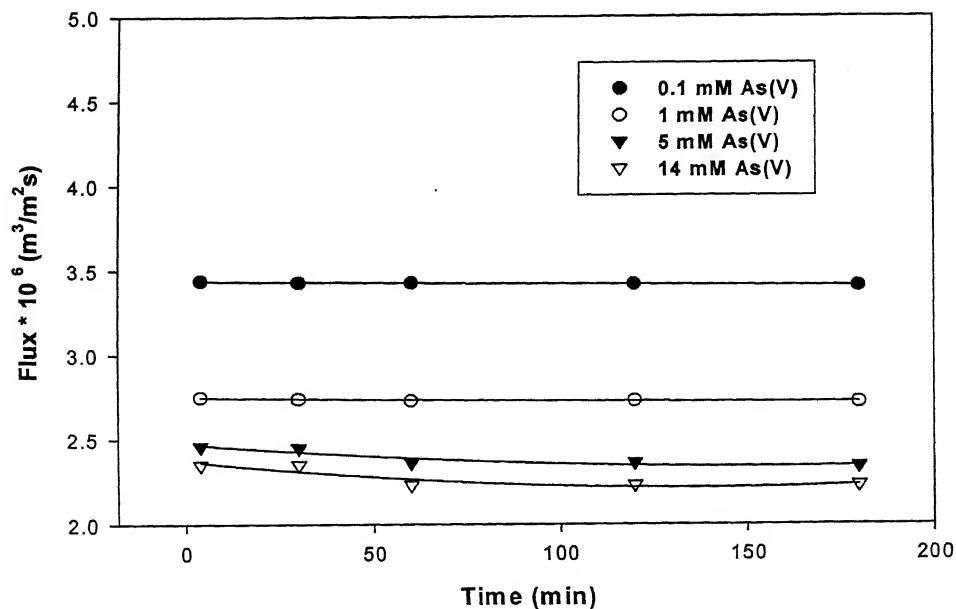


Fig. 5.17 - Flux at varying arsenate concentrations at 30 mM CPC and 689 kPa

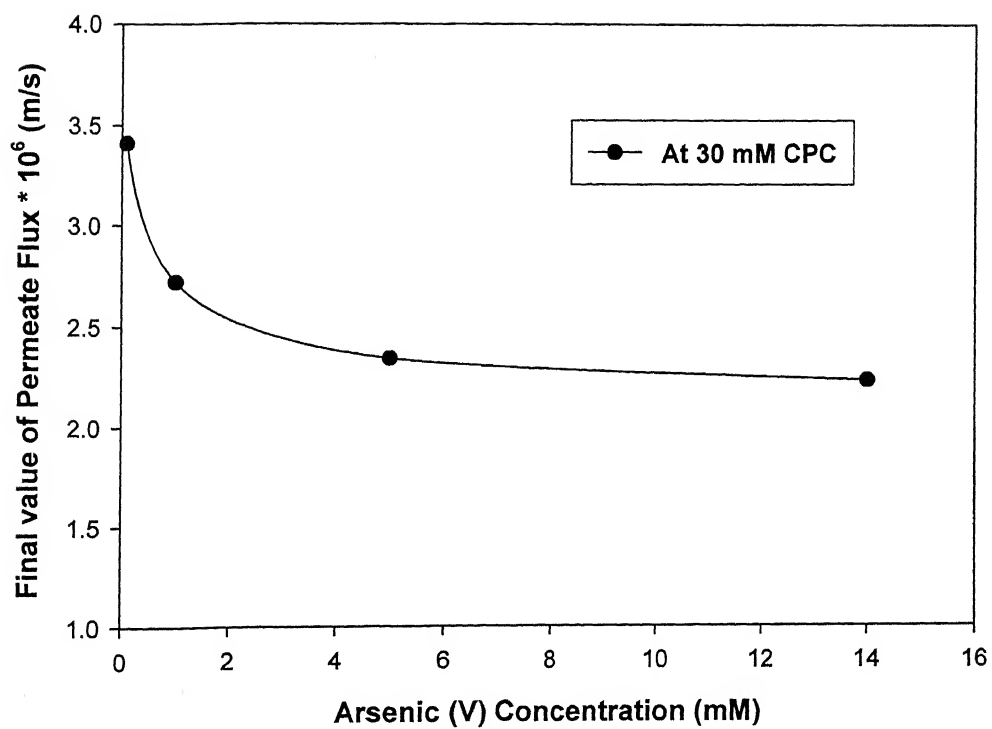


Fig. 5.18 - Permeate flux as a function of arsenic (V) concentration

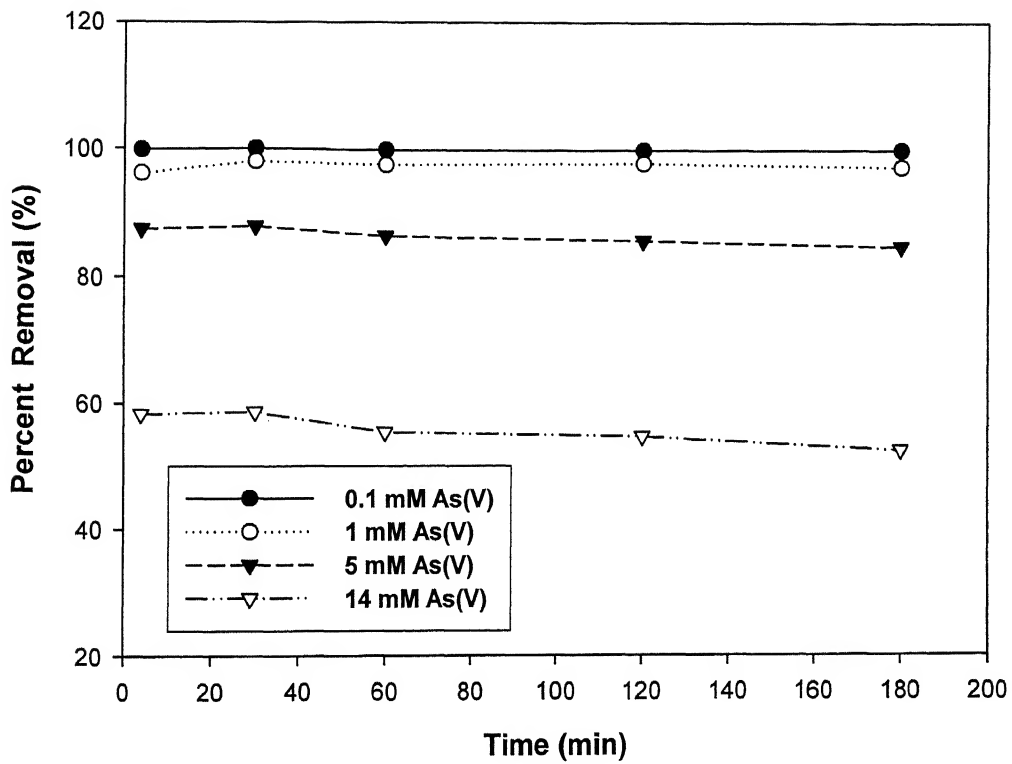


Fig. 5.19 - Variation of percentage removal with time at CPC concentration of 30 mM and 689 kPa

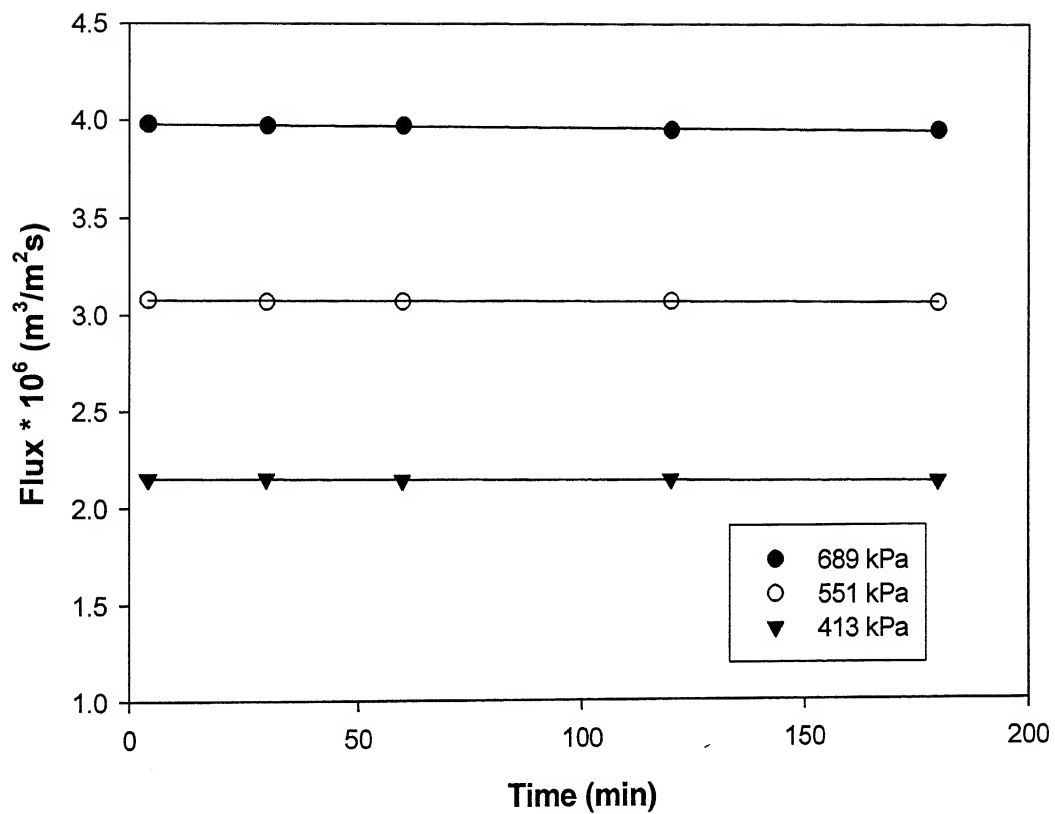


Fig. 5.20 - Flux versus time for 0.1 mM As (V) and 30 mM CPC at different pressures

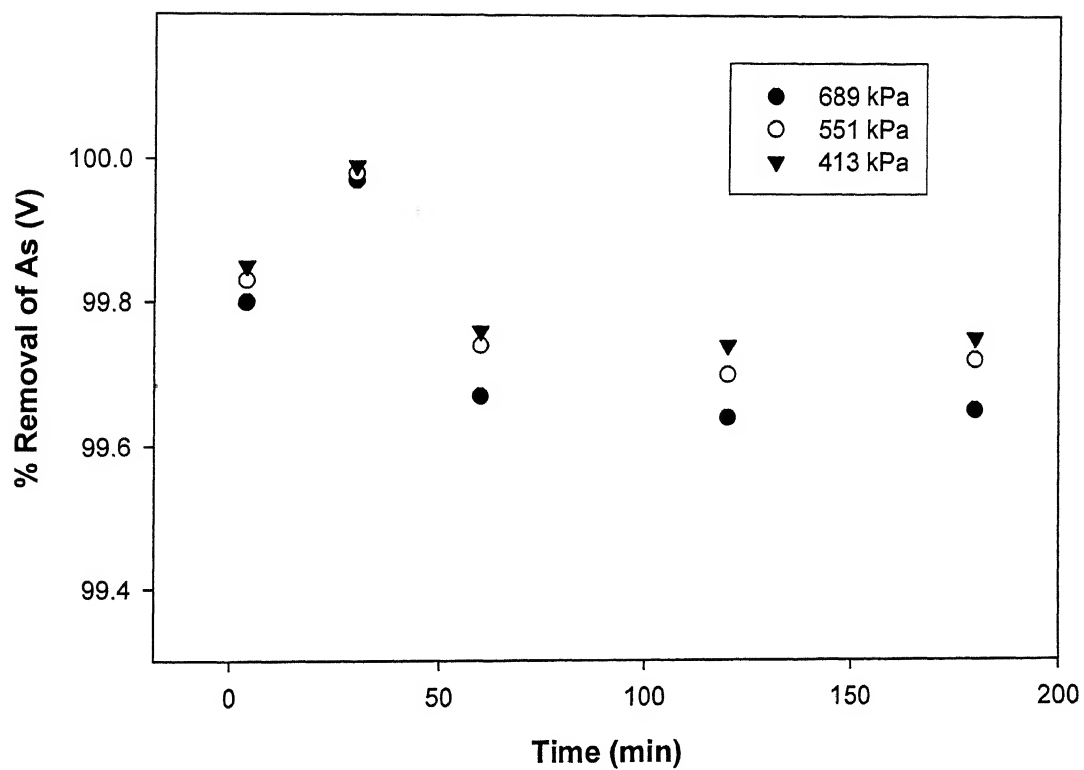


Fig. 5.21 - Variation of percent removal of As (V) = 0.1 mM with time at CPC concentration of 30 mM at different pressures

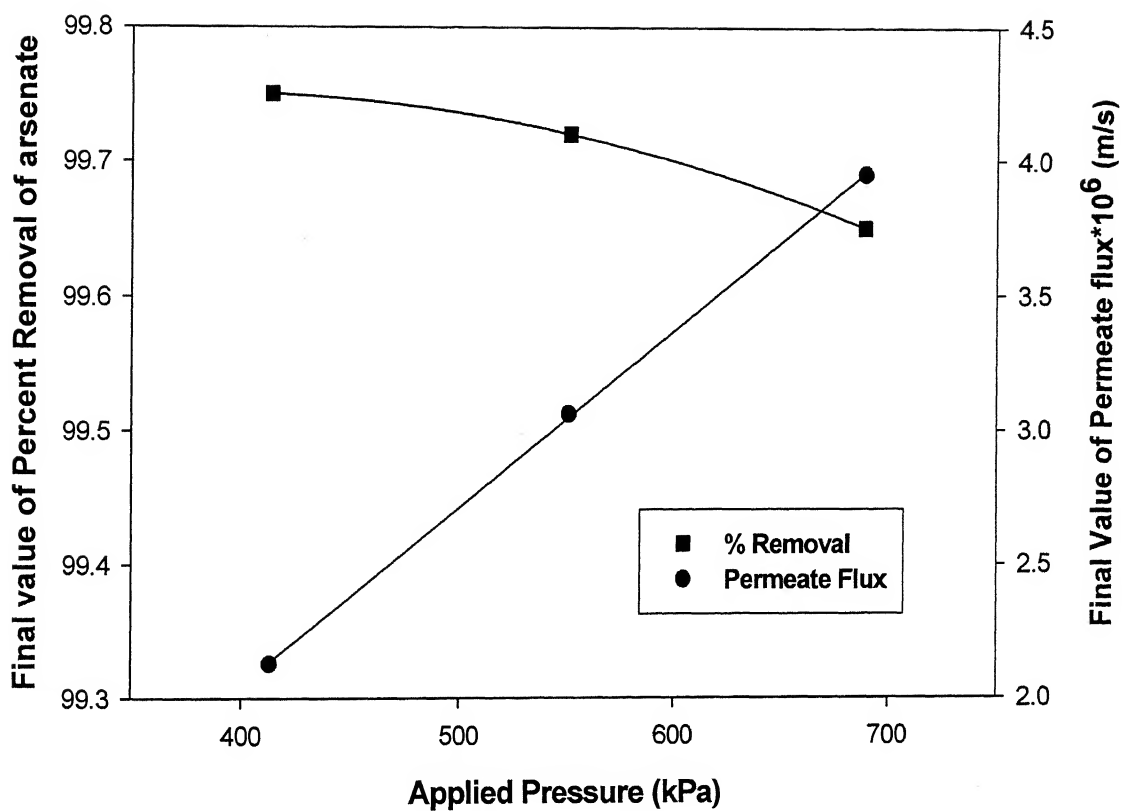


Fig. 5.22 – Percent removal and permeate flux as a function of applied pressure at 0.1 mM As (V) and 30 mM CPC

been shown earlier, there was no observance of concentration polarization, the expected linear trend was observed following simple Darcy's law.

5.4 Langmuir Adsorption

In MEUF, it is now assumed that the permeate concentration of arsenate is equal to the unadsorbed arsenate concentration in the retentate as well as adsorbed arsenate on membrane surface (considered to be negligible, which is indeed very small). Therefore, the value of adsorbed arsenic concentration and consequently the *langmuir* adsorption equilibrium constant K_s , when measured using MEUF were found slightly over-estimated (as neglecting membrane adsorption portion).

The *langmuir* adsorption equilibrium constants, according to the equation 3.22 for $n = 1$, were found out as shown in Fig.5.23. Such values can be utilized for further generating the model of the process.

The influence of feed surfactant concentration and arsenic concentration on adsorption of arsenic was observed and shown in Fig.5.24. This plot is in effect would be giving similar trends as obtained with retentions versus feed CPC concentrations. Obviously as explained, earlier the adsorption of arsenate decreased with the increase in surfactant concentration. This is because with the increase in surfactant concentration the mole fraction of micelles also increases. Larger amount of adsorbing sites being present for the arsenate, the adsorption of arsenate per unit mass of micelles decreases.

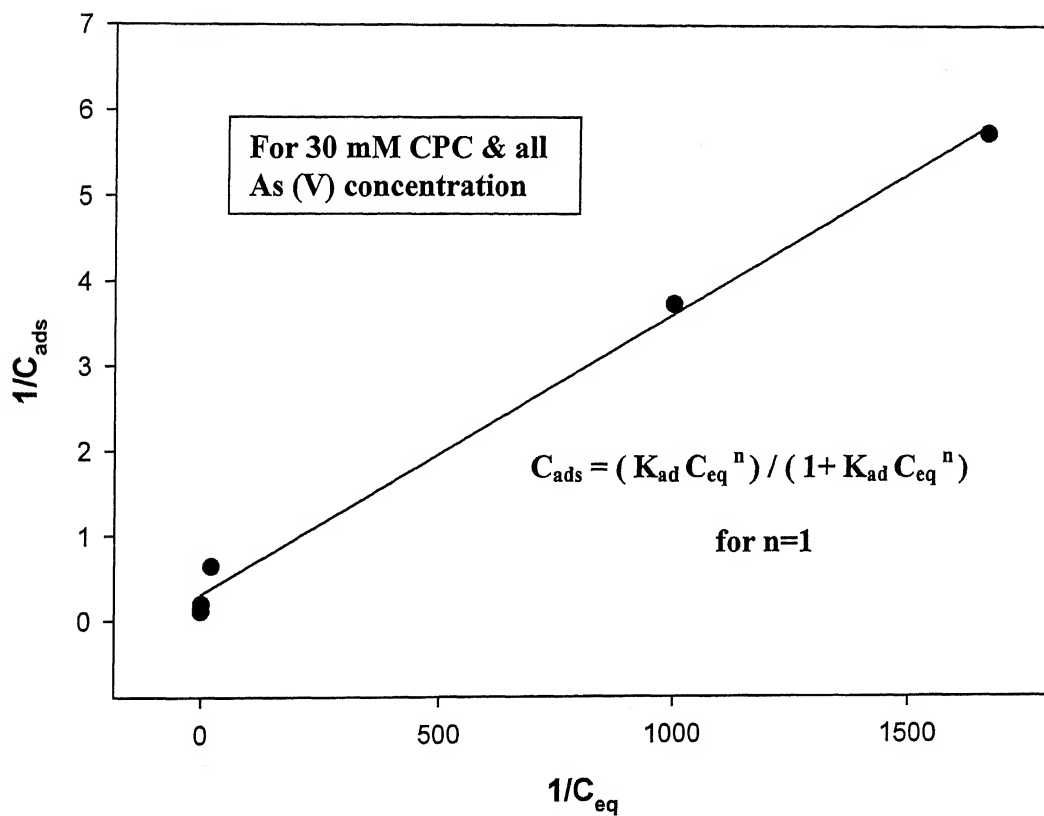


Fig. 5.23 – Langmuir plot for the adsorption of As (V) on the micelle surface

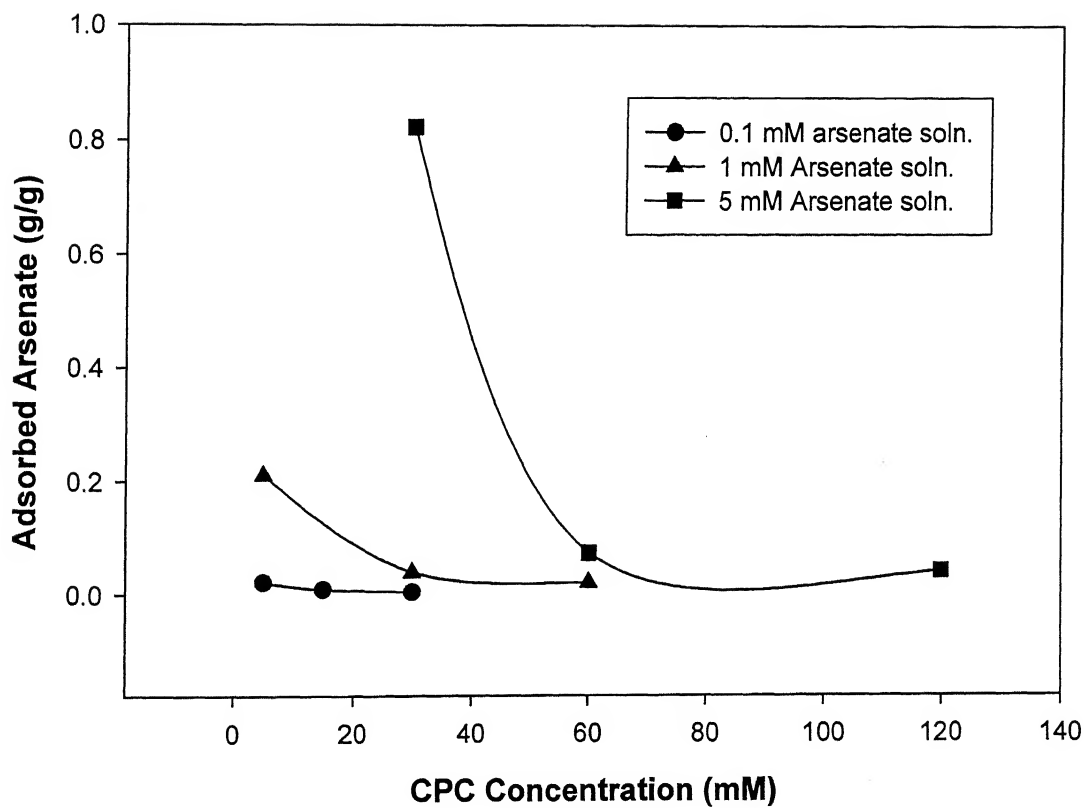


Fig. 5.24 - Adsorbed Arsenate vs. Surfactant Concentration

Conclusions and Recommendations

6.1 Conclusions

Ultrafiltration experiments were carried out with a cationic surfactant CPC in a batch cell in an unstirred pattern with 10,000 MWCO membrane. The removal of pentavalent form of arsenic [As (V)] was studied over a wide range of concentration.

Based on the study the following conclusions can be drawn:

1. Under constant applied pressure the permeate flux was found to be constant for exclusive arsenic runs [As (V)] indicating the negligible effect of concentration polarization.
2. With the increase in pressure there is a clear evidence of concentration polarization specifically during the initial period of the experimental run. However, the permeate flux is found to vary linearly with pressure, indicating insignificant development of resistance against flow at low value of arsenate concentration in feed.
3. The retention of 0.1 mM of exclusive As (V) in water decreases from 6.75 to 4.95 % with the increase in pressure from 413 to 689 kPa. Such a low retention value suggests that there may be little adsorption of arsenate on the membrane surface while most of it permeates through the membrane.
4. The retention of As (V) was found to be more as compared to the retention of As (III) at the same pH of 7.5 as arsenite [As (III)] exists in the form of H_3AsO_3 (neutral molecule) and arsenate [As(V)] exists as H_2AsO_4^- and HAsO_4^{2-} (anionic solute) in the pH range of 5-8.
5. The permeate flux was observed to decline with the increase in feed CPC concentration. The increased resistance offered by MAL to the flow may be the reason behind it.
6. The permeate concentration of CPC was found to increase with the feed surfactant concentration for a run of 0.1 mM As (V). Beyond the critical feed concentration (57mM), the permeate concentration was found to be beyond CMC. This was due to breaking of micelles into dimmers and trimers.

7. With the increase in arsenate concentration the permeate flux was found to decrease. The micelles containing metal ion being bigger produce greater resistance to flow.
8. The increase in surfactant concentration leads to an increase in percent removal. However, at very high feed surfactant concentration the percent removal reaches a saturation value.
9. The removal patterns are different for different arsenate concentrations. For very low arsenate concentration of the order 0.01 mM there is a very marginal increase in retention. for 4 mM CPC concentration; after which it declines and become less than the percentage retention obtained by 3 mM CPC solution. The micelles keep forming and breaking which therefore may saturate adsorption of arsenate per unit mass of micelles beyond an increase in the concentration of surfactant.
10. For the concentration of 0.1 mM and 1 mM arsenate, there is an initial increase in the percentage removal and then saturation was observed. If at all there were any fall in percent removal, as somewhat observed, that may be due to coupling between broken small size micelles and arsenate ions that might be permeating through the 10,000 MWCO membrane used for the purpose.
11. A perceptible decrease in retention is seen for very high arsenate concentration (14 mM) at the initial period after which more or less it remains constant. This may be due to the fact that adsorption may not be favored at this high concentration of arsenic

6.2 Recommendations

1. The study can be extended for observing the removal of trivalent form of arsenic which is the more toxic and carcinogenic form of arsenic.
2. The effect of pH on the percent removal of pentavalent arsenic can also be studied, as it is one of the most important constraint that effects the separation of arsenic.
3. The studies may be extended using different MWCO membranes and different surfactants.
4. The effect of temperature and stirring on the adsorption of arsenate ions on the micelle surface may be investigated.
5. A mathematical model can be developed further (work is in progress).

Appendix A

A1 Estimation of Hydraulic Membrane Resistance

The hydraulic membrane resistance is given by:

$$R_m = \frac{1}{\mu_w} \left(\frac{\Delta P}{J_w} \right) \quad \text{A1.1}$$

Water permeability of the membrane is given by $\left(\frac{J_w}{\Delta P} \right)$.

Using the data given in Table A1.1, the membrane resistance was found to be $1.23 \times 10^{13} \text{ m}^{-1}$ and the water permeability was 8.65×10^{-11} .

ΔP (kPa)	Water Flux $\times 10^6 \text{ (m/s)}$
482	2.94
620	4.13
758	5.31

Table A1. Water flux vs. applied pressure

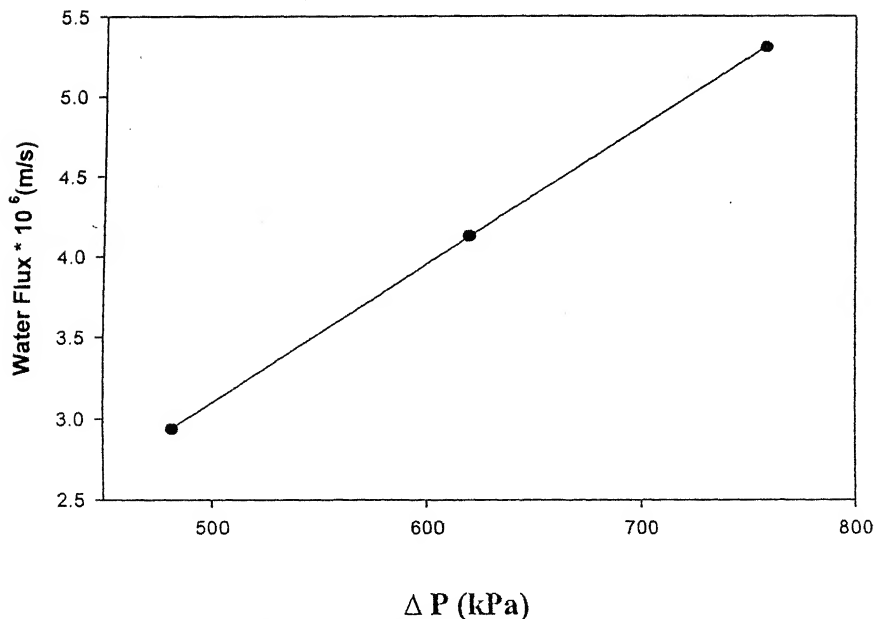


Fig. A-1 Estimation of Hydraulic Membrane Resistance

A2 Concentration measurement using UV-VIS Spectrophotometer

The permeate concentrations of CPC and pentavalent arsenate were calculated from the absorbance of the permeate samples. The absorbances were measured at wavelengths 259nm and 865nm.

The calibration curves were used for measuring the unknown concentration of the permeate sample (refer section 3.5 and 3.6). The concentration of CPC was measured directly by calling the calibration curve of CPC and the Molybdenum Blue Method measured that of As (V) at 865 nm after development of color.

Appendix B

Experimental Data of Exclusive As (V) or blank Runs

Time (min)	Permeate Flux* 10^6 (m/s)		
	$\Delta P = 413$ kPa	$\Delta P = 551$ kPa	$\Delta P = 689$ kPa
4	4.03	5.52	5.89
30	4.01	5.01	5.55
60	3.89	5.01	5.55
120	3.89	5.00	5.54
180	3.88	5.00	5.54

Table B1 Permeate Flux data for exclusive runs of As (V):0.1 mM at different pressures

Time (min)	Percent Retention		
	$\Delta P = 413$ kPa	$\Delta P = 551$ kPa	$\Delta P = 689$ kPa
4	42.6500	30.6200	29.5600
30	16.3200	9.5600	5.6500
60	6.5600	5.6500	4.2300
120	4.3200	2.1500	3.3100
180	6.7500	5.1200	4.9500

Table B2 Retention data for exclusive runs of As (V):0.1 mM at different pressures

Time (min)	Permeate Flux* 10 ⁶ (m/s)	
	As (V) = 0.1 mM at 689 kPa	As (III) = 0.1 mM at 689 kPa
4	5.8900	6.1200
30	5.5500	5.8200
60	5.5500	5.8100
120	5.5400	5.8000
180	5.5400	5.8000

Table B3 Flux data for As (V) vs. As (III) (0.1 mM) at 689 kPa

Time (min)	Percent Retention	
	As (V) = 0.1 mM at 689 kPa	As (III) = 0.1 mM at 689 kPa
4	29.5600	24.3200
30	6.6500	5.6500
60	4.2300	3.6100
120	3.3100	2.1500
180	4.9500	3.6500

Table B4 Percent Retention data for As (V) vs. As (III): 0.1 mM at 689 kPa

Appendix C

Experimental Data of MEUF Runs

Time (min)	Permeate Flux* 10 ⁶ (m/s)		
	2 mM CPC	3 mM CPC	4 mM CPC
4	4.0600	4.0400	4.0100
30	4.0600	4.0300	4.0100
60	4.0600	4.0300	4.0000
120	4.0500	4.0300	4.0000
180	4.0500	4.0200	4.0000

Table C1 Flux data for 0.01 mM As(V) at 689 kPa at different CPC Concentration

Time (min)	Percent Retention		
	2 mM CPC	3 mM CPC	4 mM CPC
4	93.5400	97.5300	97.6100
30	96.2200	98.3900	98.4300
60	96.5600	98.5800	98.5600
120	96.1300	97.3600	97.0100
180	96.0200	97.0500	97.0200

Table C2 Percent Retention data for As (V): 0.01 mM & 689 kPa at different CPC Concentration

Time (min)	Permeate Flux* 10 ⁶ (m/s)		
	5 mM CPC	15 mM CPC	30 mM CPC
4	3.9800	3.7400	3.4400
30	3.9700	3.7300	3.4300
60	3.9700	3.7300	3.4300
120	3.9500	3.7200	3.4200
180	3.9500	3.7100	3.4100

Table C3 Flux data for 0.1 mM As(V) at 689 kPa at different CPC Concentration

Time (min)	Percent Retention		
	5 mM CPC	15 mM CPC	30 mM CPC
4	88.5300	94.0030	99.8000
30	89.5400	94.4800	99.9900
60	92.6500	96.8100	99.6600
120	91.5300	96.4000	99.6400
180	90.6500	95.1800	99.6400

Table C4 Percent Retention data for As (V): 0.1 mM & 689 kPa at different CPC Concentration

Time (min)	Permeate Flux* 10 ⁶ (m/s)		
	5 mM CPC	30 mM CPC	60 mM CPC
4	3.3410	2.7500	2.1600
30	3.3400	2.7400	2.1500
60	3.3300	2.7300	2.1500
120	3.3300	2.7300	2.1400
180	3.3300	2.7200	2.1300

Table C5 Flux data for 1 mM As(V) at 689 kPa at different CPC Concentration

Time (min)	Percent Retention		
	5 mM CPC	30 mM CPC	60 mM CPC
4	91.3600	96.0600	99.5300
30	92.5800	97.9600	99.8600
60	92.0100	97.3600	98.9200
120	92.0600	97.5600	99.3500
180	92.3800	96.9600	99.1700

Table C6 Percent Retention data for As (V): 1 mM & 689 kPa at different CPC Concentration

Time (min)	Permeate Flux* 10 ⁶ (m/s)		
	30 mM CPC	60 mM CPC	120 mM CPC
4	2.4600	1.8800	1.5510
30	2.4500	1.8800	1.5510
60	2.3600	1.7600	1.4300
120	2.3600	1.7500	1.4200
180	2.3400	1.7400	1.4100

Table C7 Flux data for 5 mM As(V) at 689 kPa at different CPC Concentration

Time (min)	Percent Retention		
	30 mM CPC	60 mM CPC	120 mM CPC
4	77.8600	87.3600	98.1280
30	78.1500	87.7900	98.7500
60	77.6600	86.2100	98.0200
120	77.0100	85.4500	97.7900
180	76.4300	84.4300	97.0200

Table C8 Percent Retention data for As (V): 5 mM & 689 kPa at different CPC Concentration

Time (min)	Permeate Flux* 10 ⁶ (m/s)				
	5 mM CPC	30 mM CPC	60 mM CPC	120 mM CPC	240 mM CPC
4.0000	2.8300	2.3500	1.7600	1.4010	1.0500
30.0000	2.8300	2.3500	1.7600	1.4010	1.0500
60.0000	2.6800	2.2300	1.6400	1.2630	0.9200
120.0000	2.6800	2.2300	1.6400	1.2630	0.9200
180.0000	2.6800	2.2300	1.6400	1.2630	0.9200

Table C9 Flux data for 14 mM As(V) at 689 kPa at different CPC Concentration

Time (min)	Percent Retention				
	5 mM CPC	30 mM CPC	60 mM CPC	120 mM CPC	240 mM CPC
4.0000	57.0300	58.2500	60.6900	80.7000	92.9900
30.0000	51.8620	58.6000	60.2500	71.7300	84.2600
60.0000	48.4300	55.3500	58.4000	72.2040	84.2500
120.0000	46.6800	54.6500	58.2000	70.8400	84.6000
180.0000	35.8400	52.3600	60.9000	72.5600	85.7400

Table C10 Percent Retention data for As (V): 14 mM & 689 kPa at different CPC Concentration

Appendix D

Experimental Data of MEUF Runs at constant CPC concentration (30 mM)

Time (min)	Permeate Flux* 10^6 (m/s)			
	0.1 mM As (V)	1 mM As (V)	5 mM As (V)	14 mM As (V)
4.0000	3.4400	2.7500	2.4600	2.3500
30.0000	3.4300	2.7400	2.4500	2.3500
60.0000	3.4300	2.7300	2.3600	2.2300
120.0000	3.4200	2.7300	2.3600	2.2300
180.0000	3.4100	2.7200	2.3400	2.2300

Table D1 Permeate Flux data for different arsenate conc. at 30 mM CPC and 689 kPa

Time (min)	Permeate Flux* 10^6 (m/s)			
	0.1 mM As (V)	1 mM As (V)	5 mM As (V)	14 mM As (V)
4.0000	99.8000	96.0600	87.3600	58.2500
30.0000	99.9900	97.9600	87.7900	58.6000
60.0000	99.6700	97.3600	86.2100	55.3500
120.0000	99.6400	97.5600	85.4500	54.6500
180.0000	99.6500	96.9600	84.4300	52.3600

Table D2 Percent Retention data for different arsenate conc. at 30 mM CPC and 689 kPa

Feed CPC concentration 30 mM		
Concentration of As (V)	Final value of Permeate Flux*10 ⁶ (m/s)	Final value of Percent Retention of As (V)
0.1000	3.4100	99.6500
1.0000	2.7200	96.9600
5.0000	2.3400	84.4300
14.0000	2.2300	52.3600

Table D3 Permeate Flux and Percent Removal vs. Concentration of As (V) at 30 mM CPC and 689 kPa pressure

Time (min)	Feed CPC concentration of 30 mM and As (V) = 0.1 mM		
	$\Delta P = 413 \text{ kPa}$	$\Delta P = 551 \text{ kPa}$	$\Delta P = 689 \text{ kPa}$
4.0000	3.9800	3.0800	2.1500
30.0000	3.9700	3.0700	2.1500
60.0000	3.9700	3.0700	2.1400
120.0000	3.9500	3.0700	2.1400
180.0000	3.9500	3.0600	2.1300

Table D4 Permeate Flux data for different operating pressures at 30 mM CPC and 0.1 mM As (V)

Feed CPC concentration 30 mM		
Different pressures	Final value of Permeate Flux*10 ⁶ (m/s)	Final value of Percent Removal of As (V)
$\Delta P = 413 \text{ kPa}$	2.1300	99.7500
$\Delta P = 551 \text{ kPa}$	3.0600	99.7200
$\Delta P = 689 \text{ kPa}$	3.9500	99.6500

Table D5 Permeate Flux and Percent Removal of As (V) at 30 mM CPC and different operating pressures

Appendix E

Adsorption equilibrium constants calculated with MEUF Data for 30 mM CPC and all As (V) concentration

1/Ceq (mM)	1/Cads (mM)
1666.6700	5.7300
1000.0000	3.7310
22.1700	0.6413
0.6300	0.1940

Table E1 Calculation of K_{ad} for 30 mM CPC Concentration by Langmuir Adsorption Isotherm

CPC conc. (mM)	K_{ad} (ml/g) (dimensionless)	Regression Coefficient
5	9.68	0.997
30	303.33	0.9944
60	865.35	0.9913

Table E2 Variation of K_{ad} with surfactant concentration

Appendix F

Physical Property	Value
Diffusivity of CPC	$1.8 \times 10^{-10} \text{ (m}^2\text{/s)}$
Critical micelle conc. of CPC in 0.01M NaCl	$8.8 \times 10^{-4} \text{ M} = 0.3 \text{ kg/m}^3$
Aggregation number of CPC	136 monomers/micelle
Monomer hydrodynamic radius	0.42 nm
Micelle hydrodynamic radius	2.5 nm

Table F1 Physical constants of surfactant

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